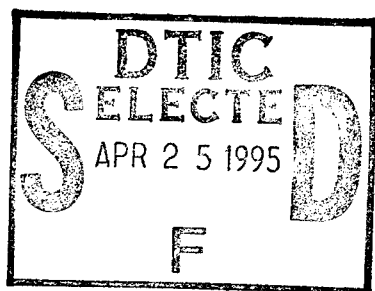**US Army Corps
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Waterways Experiment
Station

Ultraviolet/Chemical Oxidation Treatment of RDX-Contaminated Waters at Picatinny Arsenal

by   Elizabeth C. Fleming, R. Mark Bricka, Steven R. Bailey

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Prepared for   Picatinny Arsenal

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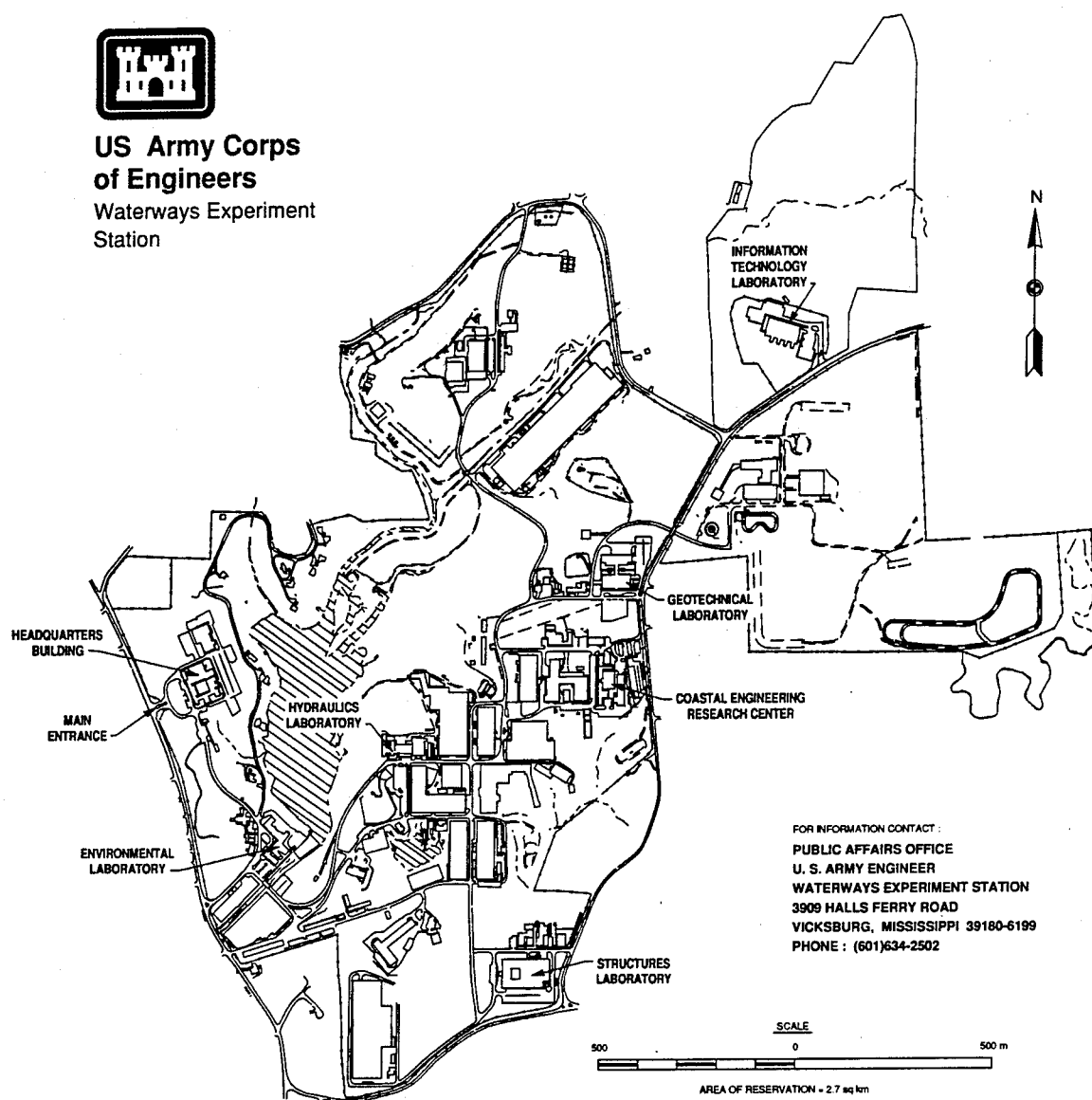3909 Halls Ferry Road
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WATERWAYS EXPERIMENT STATION
3909 HALLS FERRY ROAD
VICKSBURG, MISSISSIPPI 39180-6199
PHONE : (601)634-2502**

STRUCTURES
LABORATORY

SCALE

500   0   500 m

AREA OF RESERVATION = 2.7 sq km

Contents

List of Figures

List of Tables

Preface

The work reported herein was conducted for the Picatinny Arsenal under Military Interdepartmental Purchase Request W81EWF-2-M119. Mr. Fred Haber and Ms. Lynn Krupacs were Project Managers for the Picatinny Arsenal. This study was conducted as a bench- and pilot-scale evaluation of ultraviolet/chemical oxidation (UVChO) treatment of cyclotrimethylene-trinitramine contamination of water at the Picatinny Arsenal.

The pilot-scale evaluation of UVChO was supported, facilitated, and coordinated through the cooperation and efforts of the Armament Research and Development Engineering Center, Chief of Division of Engineering and Housing, Mr. Ron Kraus, and Installation Support Activity Water Treatment Plant Operator, Roy Oakes, and their Utilities and Operations staff.

This report was prepared by Ms. Elizabeth C. Fleming and Messrs. R. Mark Bricka and Steven R. Bailey, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Environmental Laboratory (EL), U.S. Army Engineer Waterways Experiment Station (WES). Chemical analyses were performed by Arthur D. Little (ADL) Laboratories, Cambridge, MA, and Ms. Ann Strong, Chief, Environmental Chemistry Branch, EED.

The study was conducted under the direct supervision of Mr. Daniel A. Averett, Chief, ERB, and under the general supervision of Mr. Norman R. Francinques, Chief, EED, and Dr. John W. Keeley, Director, EL.

Dr. Robert W. Whalin was Director of WES. COL Bruce K. Howard, EN, was Commander.

This report should be cited as follows:

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
acres	4,046.873	square meters
cubic feet	0.02831685	cubic meters
degrees Fahrenheit	5/9	degrees Celsius or kelvins[1]
feet	0.3048	meters
gallons (U.S. liquid)	0.003785412	cubic meters
inches	0.0254	meters
miles (U.S. statute)	1.609347	kilometers
pounds (mass)	0.4535924	kilograms

[1] To obtain Celcius (C) temperature readings from Fahrenheit (F) readings, use the following formula: C = (5/9)(F - 32). To obtain kelvin (K) readings, use: K = (5/9)(F - 32) + 273.15.

1 Introduction

Background

The Picatinny Arsenal is located just north of Dover, New Jersey, approximately 40 miles[1] west of New York City, NY (see Figure 1). Between 1976 and 1989, the Picatinny Arsenal and the U.S. Army Environmental Center (USAEC) identified 156 remedial investigation sites at the Arsenal. Due to the production and testing of explosives in some areas at the site, the drinking water supply at the Picatinny Arsenal has been contaminated with low levels of cyclotrimethylene-trinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX).

Site 138 in Area F, shown in Figure 2, contains drinking water supply well 410 and well 430A and was the location of chemical laboratories and propellant plants. In the 1980s, sampling of well 410 revealed low-level contamination of trichloroethylene (TCE), RDX, and HMX. Well 430A was reported to be free of contamination by volatile organic compounds (Foster Wheeler Enviresponse, Inc. 1990).

Area F comprises 17 individual contaminated sites and covers approximately 86 acres and has historically been used for the processing, mixing, and utilization of propellants. Building 408, also located in site 138, was reportedly used for explosives metal casting and chemical synthesis operations. Compounds such as lead azide, mercury fulminate, trinitrotoluene (TNT), HMX, and RDX have been synthesized there. Wastewater generated from these operations was reportedly discharged into a nearby swamp. The closest well to Building 408 is 410, which is approximately 300 ft upgradient from the swampy areas behind Building 408. Well 430A is more than 800 ft from and at an equal gradient to the same swamp (Foster Wheeler Enviresponse, Inc. 1990). Drinking supply well 410 is located at the intersection of Ninth Street and Sixteenth Avenue. Well 410 takes water from the water table or unconfined stratified drift aquifer.

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[1] A table of factors for converting non-SI units of measurement to SI units is presented on page viii.
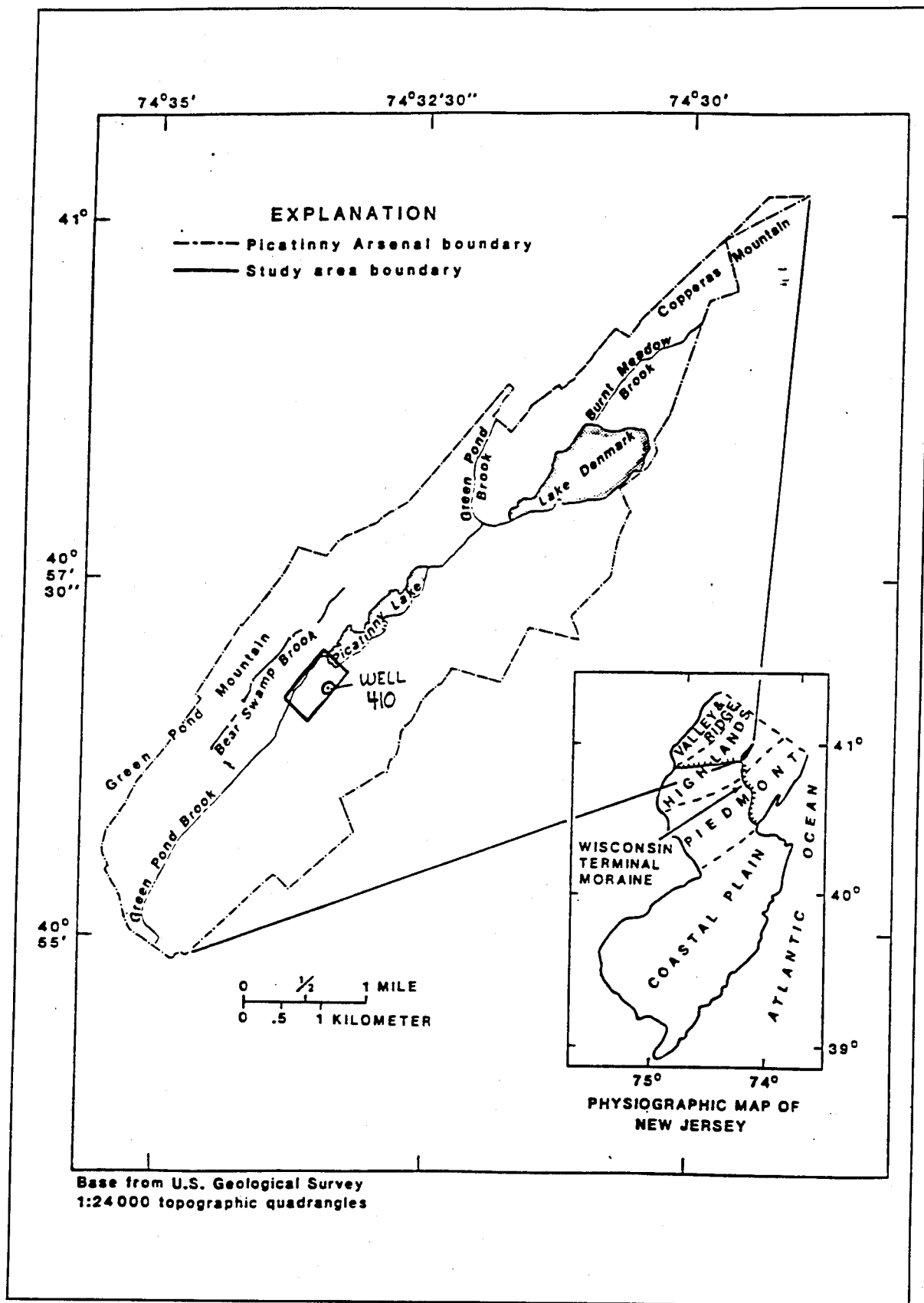
Figure 1.   Location of Picatinny Arsenal

LEGEND:

⊕ Existing Monitoring Well Location

⬤ Proposed Monitoring Well Location

↗ Inferred Direction of Shallow Groundwater Flow

- - - AREA F

AREA F
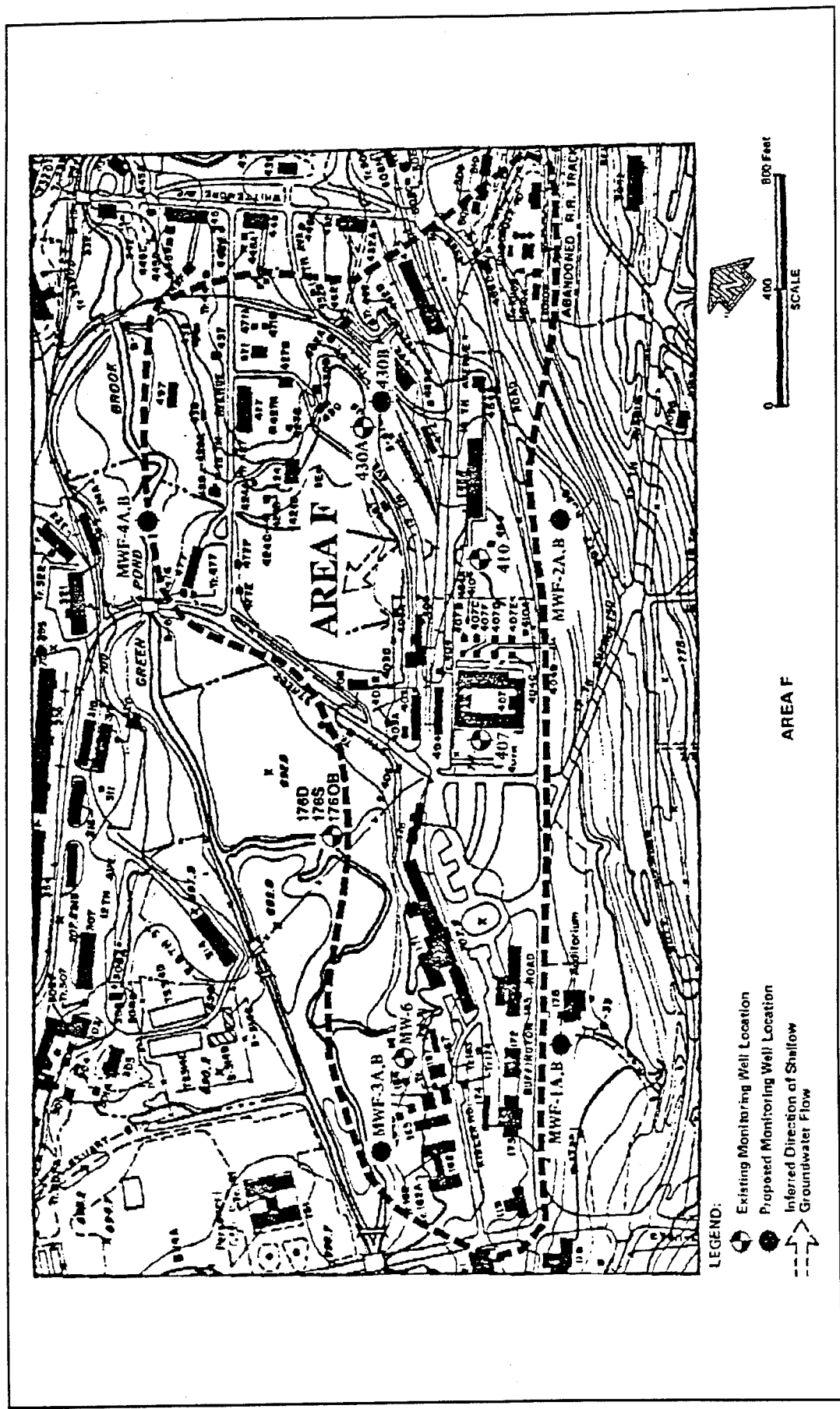
Figure 2. Location of Site 138, Building 408, and Well 410

The aquifer is within 15 ft of the ground surface and extends to a depth of 100 ft below the ground surface. The soils at the site consist of well-drained deposits of gravels and sands. During normal operations, well 410 produces 300 to 320 gpm. The water pumped from wells 410 and 430A flows to a drinking water treatment plant, Building 1383, where it is routed to green sand filters after addition of potassium permanganate for removal of iron and manganese. After the sand filters, the water goes to an air stripper for volatile organic compound (VOC) removal, specifically TCE, followed by pH control and chlorination, before being distributed to the potable water system. The water is thus distributed at or below the primary maximum concentration level for TCE concentration in drinking water, 1 μg/L (Foster Wheeler Enviresponse, Inc. 1990). In the 1980s, RDX and HMX were below health advisory levels. Since then, health advisory levels were lowered (November 1988) by the U.S. Environmental Protection Agency (USEPA) and are 2 μg/L and 400 μg/L for RDX and HMX, respectively. The health advisory standards are expected to be adapted as new drinking water standards. TCE and RDX concentrations in well 410 have been reported to range from 1.0 μg/L to 13.6 μg/L and 4.4 μg/L to 6.3 μg/L, respectively. HMX concentrations are approximately 2 μg/L, well below the health advisory standard of 400 μg/L, but RDX concentrations have exceeded the lifetime health advisory standard of 2 μg/L.

Responding to the situation, the Picatinny Arsenal requested that the U.S. Army Engineer Waterways Experiment Station (WES) evaluate two technologies for removal of RDX, ultraviolet/chemical oxidation (UV/ChO) and granular activated carbon (GAC) adsorption. Both treatment technologies were evaluated on the bench- and pilot-scale levels. The WES Environmental Chemistry Branch (ECB) and Arthur D. Little (ADL), Cambridge, MA, performed the analyses of the treated and untreated samples. This report presents information pertinent to the UV/ChO study; the GAC adsorption test procedures and results are presented in a separate report (Bricka and Fleming, in preparation). Preliminary screening tests and pilot-scale tests were conducted at the Picatinny Arsenal. The bench-scale tests were conducted at the WES Hazardous Waste Research Center (HWRC) in Vicksburg, MS.

UV/Chemical Oxidation

Background

Because of the concern for trading one environmental problem for another, UV/ChO is becoming a more popular method of treatment for contaminated waters. Instead of transferring contaminants from one medium to another, UV/ChO destroys the contaminant with little or no air emissions.

4

UV/ChO involves the use of oxidants such as ozone and hydrogen peroxide to destroy organic contaminants. A product of decomposition of these two oxidants is hydroxyl radicals that have strong oxidizing powers. The ChO processes that result in hydroxyl radical formation are generally referred to as advanced oxidation processes (AOP). The hydroxyl radicals attack organic species by abstracting a hydrogen atom or adding to the double bond of unsaturated molecules. UV light used as a catalyst can increase the rate of hydroxyl radical formation. Hydroxyl radicals are less selective oxidizers than ozone, UV light, or hydrogen peroxide alone, allowing them to destroy a wider variety of contaminants (Roy 1990). UV refers to a range of radiation wavelengths shorter than those in the visible spectrum and longer than those in the X-ray region (Roy 1990). Ideally, the hydroxyl radicals combine with organic constituents to convert organics to carbon dioxide, water, oxides of nitrogen and other oxides, or carboxylic acids (Cheremisinoff 1989). In UV/ChO treatment, several types of chemical degradation may occur and are described below in the order of increasing desirability (Bowers et al. 1989).

a. Primary Degradation—a structural change in the parent compound.

b. Acceptable Degradation—degradation to the extent that toxicity is reduced.

c. Ultimate Degradation—complete destruction to CO_2, H_2O, or other inorganics, or organic acids such as carboxylic acid.

The residence time required for destruction can be decreased in some cases by the addition of UV light as well as other chemical catalysts. Residence time refers to the theoretical amount of time a particle of water is in the reactor, from the entry to the exit point, based upon the volume of the reactor and the water flowrate. Catalysts can be used to change the speed of a reaction without affecting the products of UV/ChO. With the addition of catalysts, the products are the same; only the rate of approach to equilibrium is changed because the catalyst will act to speed up the rate of reaction. The solution has reached the equilibrium point when there is no net change in the constituents. An example of the change in reaction rates by addition of catalysts is illustrated in Figure 3 (Breschia et al. 1980).

An example of a catalyzed reaction is the addition of titanium dioxide or tungsten oxide (used in the preliminary evaluation). In the presence of a semiconductor solid such as titanium dioxide or tungsten oxide, the photons must possess energies of bandgap magnitude, less than 1 eV. Such excitation produces conduction band electrons and valence band holes, which can migrate to the liquid/solid interface to participate in charge transfer (Yue 1990). There are two types of catalysts, homogeneous and heterogeneous. In homogeneous catalysis, the reaction occurs in one phase. In heterogeneous catalysis, the reaction occurs in steps and usually involves a solid catalyst. It is not easy to determine the mechanism of heterogeneous catalysts or to find the rate-determining step because heterogeneous catalysis involves:
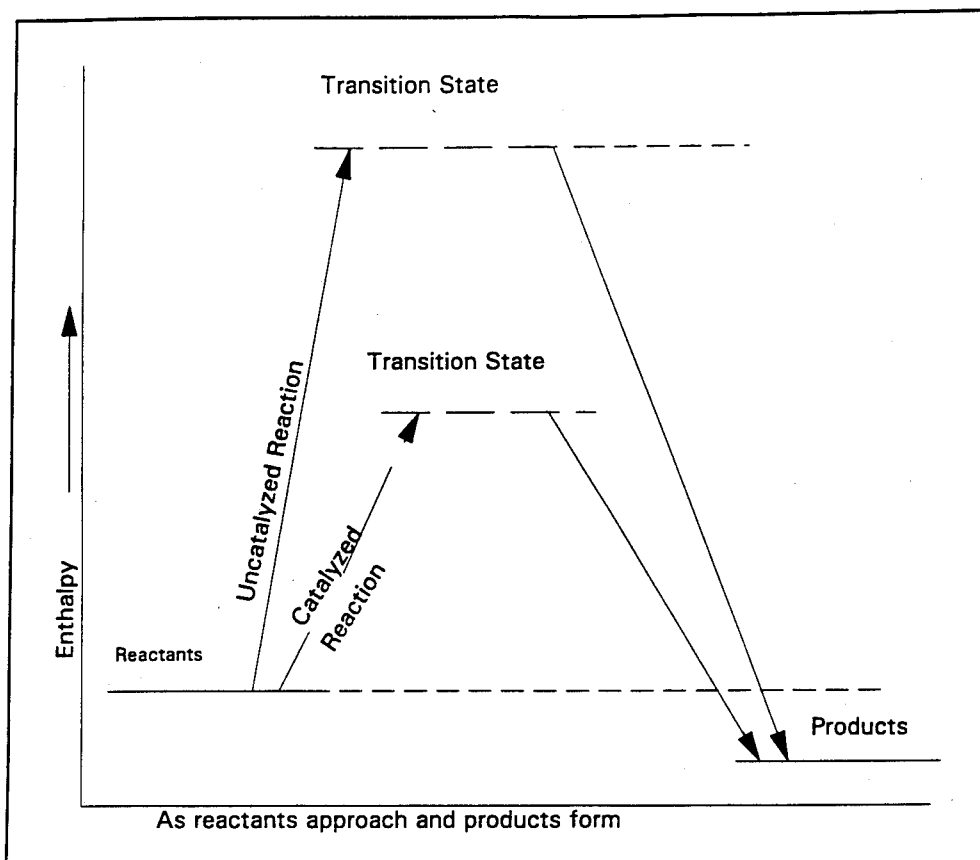
Figure 3.   Change in reaction rates by addition of catalysts

a. Diffusion of reactants to the surface of the catalyst.

b. A reaction between the molecules of the reactants and the atoms in the surface of the solid catalyst (adsorption).

c. Reaction between adsorbed molecules.

d. Separation of the products from the surface (desorption).

RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazine) molecules are illustrated below. HMX concentrations in well 410 water were well below the health advisory of 400 μg/L and will not be discussed further. At Building 1383, the point of distribution, concentrations of HMX have been maintained at or below 3 μg/L by blending the raw water sources. In the bench-scale studies, analysis of well 410 water indicated that RDX concentrations ranged from 3.2 μg/L to 4.80 μg/L, above the health advisory level of 2 μg/L. RDX is formed by the reaction of nitric acid with methenamine and is practically insoluble in water. RDX is classified as a secondary high explosive and an EPA Group C compound: Possible Human Carcinogen (McLellan, Hartley, and Brower 1988). The density of RDX is 1.0 g/cc (Cook 1966). The structure of the RDX molecule indicates that any one of the three types of degradation described above is possible. Primary degradation may occur by
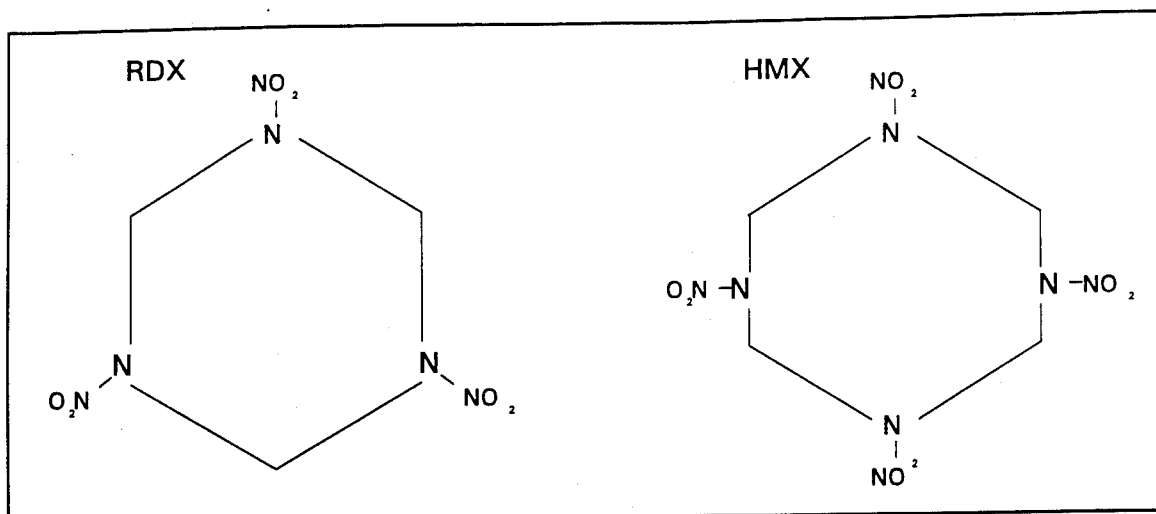
the partial breakdown of the ring, acceptable degradation by formation of intermediates that are not toxic, or ultimate degradation by breakdown of RDX and HMX to CO_2, H_2O, and NO_2. Ultimate degradation is desirable but is not always attainable. For example, the destruction of chloroform, $CHCl_3$, involves complex reactions as illustrated below (Cater et al. 1989). Equations 1, 2, and 3 represent primary, acceptable, and ultimate degradation, respectively.

$$CHCl_3 + {-}OH \rightarrow H_2O + {-}CCl_3 \rightarrow {-}CCl_3O_2 \rightarrow CCl_3O_2{-} + HCO_3 \qquad (1)$$

$$\downarrow H_2O_2 \qquad \downarrow H_2O$$

$$HCl + {-}OH + [COCl_2] \quad [COCl_2] + HCl + HO_2{-} \qquad (2)$$

$$\downarrow H_2O \downarrow$$

$$2HCl + CO_2 \qquad (3)$$
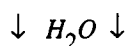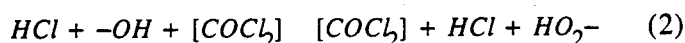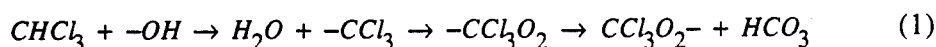
As is illustrated in the equations for degradation of chloroform, the reaction pathways are complex and ultimate destruction is not always attained.

Vendors

There are a number of commercial vendors that market proprietary UV/ChO methods. The primary vendors are listed below.

a. Ultrox, Inc.

b. Peroxidation Systems, Inc.

c. Solarchem, Inc.

    d. Excalibur Enterprises, Inc.

    e. Nutech, Inc.

    f. Purus, Inc.

Most vendor systems utilize plug flow reactors, in which there is no mixing in the direction of flow and complete mixing perpendicular to the direction of flow. Theoretically, each element of fluid passing through the reactor resides in it for the same period of time. The Ultrox process involves a combination of low-pressure UV light, 65 W, ozone, and hydrogen peroxide. Peroxidation Systems, Inc., uses a combination of medium-pressure UV light, 30 kW, and hydrogen peroxide with similar operating costs to those of Ultrox. The Solarchem process uses a 30 kW lamp, with approximately 30 percent of the output below 300 nm. Excalibur Enterprises, Inc., uses 16-W UV light, ozone, and ultrasound that aids in elimination of scaling problems. Scaling results from high iron concentrations, high suspended solids, and alkalinity which precipitate when oxidized and form scale on the quartz tube housing the UV lamps. An alternative to ultrasound for removal of solids, alkalinity, or iron is pretreatment of waters before UV/ChO. Ultraviolet Energy Generators, Inc., uses a 5-kW UV light only, which consists of a pulsing, proprietary source of deep UV light. UV light is used to dissociate, or decompose, contaminants directly. Wavelengths produced by the generator cover the entire spectrum from 190 to 600 nm, whereas most conventional systems rely on one wavelength, 254 nm. Purus, Inc., uses a pulsed-plasma xenon flashlamp that emits high-energy, high-intensity UV light that can destroy organics by direct photolysis, sometimes eliminating the need for chemical oxidizers. Direct photolysis destruction of organics is possible if sufficient UV light energy is absorbed by the target compound. The plasma is produced by a discharge of electrical energy between two electrodes. The peak UV emission is about 230 nm.

UV light sources

There are two types of lamps typically used in UV/ChO systems, low-pressure mercury and medium-pressure mercury lamps. Low-pressure mercury lamps emit the vast majority of their radiation spectrum at the 254-nm wavelength. Medium-pressure lamps emit over a wide band from approximately 190 nm to 600 nm. Typical costs for lamps range from $50 to $60 each, with an approximate one-year service life (Fahey 1990). Lamps lose approximately 30 to 40 percent of their intensity with age. UV/ChO systems operated with ozone are better served using low-pressure UV lamps (Zappi et al. 1992). Ozone has an optimum photon adsorptive capacity at the 254-nm wavelength. Conversely, hydrogen peroxide adsorbs at 200-230 nm, which is in the spectrum emitted by medium-pressure lamps. Medium-pressure lamps are much more energy intensive than low-pressure UV lamps. Much of the electrical energy utilized by medium-pressure UV lamps is wasted as heat radiation. However, some benefit

may be derived from using a medium-pressure lamp because of direct photolysis of photoreactive compounds (Zappi et al. 1992). Some systems using UV light alone, referred to as photolysis systems, are effective when the contaminants are photoreactive. Technologies using UV light harness energy from radiation wavelengths of the ultraviolet region of the spectrum, effecting chemical changes in contaminants (Roy 1990). Organics absorb the UV light, bringing their electrons to a higher energy level, making the organic more susceptible to hydroxyl radicals. The rate of photolysis is proportional to the rate of light adsorption by the compound and the quantum yield of photolysis. The quantum yield refers to the number of molecules photolyzed per photon of light absorbed (Cater et al. 1989). Depending upon the photoreactive properties of a compound, low-pressure lamps which use 254-nm wavelengths and medium-pressure lamps which emit at a range of 190 nm to 600 nm are selected. Based on lamp cost per kilowatt output, Peroxidation Systems, Inc., determined that low-pressure lamps may cost $2,200 to $3,000 and medium-pressure lamps may cost $90 to $220. However, medium-pressure lamps require 30 kW power while low-pressure lamps require 65 watts power.

Chemical oxidants

Typical oxidizers used in water treatment are hydrogen peroxide, ozone, chlorine, potassium permanganate, and sodium hypochlorite. For destruction of compounds through UV/ChO, two oxidants are used more frequently than the others, hydrogen peroxide and ozone. These oxidants more readily form hydroxyl radicals, which are the primary mechanism for contaminant destruction. For example, UV light reacts with hydrogen peroxide, creating hydroxyl radicals. The hydroxyl radicals have a more powerful oxidation potential than UV photolysis alone (Yue 1990). The photolysis by UV light makes the contaminant more susceptible to hydroxyl reactions. The molecule under UV radiation yields two hydroxyl radicals according to the following equation:

$$H_2O_2 \; ----------\rightarrow \; 2OH^{\bullet} \tag{4}$$

Hydrogen peroxide is a liquid solution, usually manufactured and sold as 30-percent to 50-percent solutions, and is generally pumped into the reactor at a specific concentration. Ozone is diffused into solution in a gaseous form, and concentrations are variable. Constant concentrations cannot be maintained due to the nature of ozone absorption/decomposition reactions in solution. Maximum ozone solubility has been identified as 21 mg/L according to Lange's Handbook of Chemistry (Dean 1985). Theoretical and experimental results obtained by Kuo et al. (1976) indicate that it is difficult to achieve a saturation concentration of absorbed ozone in solution during absorption because of depletion due to decomposition reactions, the kinetics of ozone decomposition being of a three-halves order with respect to ozone concentration. Three-halves order generally occurs when the concentration-dependent term, in this case ozone, is in

the denominator and the reaction represents a sequence of several elementary steps.

The relative oxidation potentials of the oxidants are listed in decreasing order: hydroxyl radical > ozone > hydrogen peroxide > permanganate > chlorine. Chlorine and hypochlorite addition increases Cl^- concentrations which may contribute to the formation of undesirable compounds. In a study conducted by Peroxidation Systems, Inc., the cost per pound of ozone was $0.60-$1.10 and for H_2O_2 was $0.75-$1.50 (Froelich 1992).

Catalysts

Catalysts are used to increase the speed of a reaction without changing the reaction products. Typical catalysts used for UV/ChO are Fenton's reagent, Milas's reagent, tungsten oxide, titanium dioxide, osmium tetroxide, and cadmium sulfide. Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron which increases the rate of production of hydroxyl radicals (Sedlak and Andren 1991).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^- \tag{5}$$
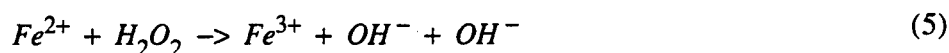
Hydroxyl radicals are then available to attack the organic species. Milas's reagent is a mixture of hydrogen peroxide in tert.-butanol, catalysed by osmium tetroxide (Cook and Schoental 1949). Milas determined that olefins, a class of unsaturated hydrocarbons, are not attacked by a solution of hydrogen peroxide without addition of osmium tetroxide (Cook and Schoental 1949). Milas reagents involve the direct conversion of unsaturated compounds into glycols, a process referred to as hydroxylation. Milas determined that oxidation by osmium tetroxide-catalysed hydrogen peroxide involves attack by free hydroxyl radicals (Mugdan and Young 1949). Metal oxide catalysts such as tungsten oxide, titanium dioxide, osmium tetroxide, and cadmium sulfide act as semiconductors when illuminated by UV light. Excited-state electron and hole pairs are produced, which are capable of initiating a wide variety of chemical reactions (Kormann, Bahnemann, and Hoffman 1991), including destruction of organics. In a study conducted by Jody, Klein, and Judeikis (1989), UV/ozone systems using tungsten catalyst were the optimal method of treating hydrazine-contaminated waters. The hydrazine contaminated waters treated with UV/ozone systems using tungsten catalyst produced an effluent with fewer intermediates than UV/ozone alone.

Full-scale systems

Full-scale systems can range in size but are generally 2,000 gal. A schematic diagram of a typical UV/ChO system is presented in Figure 4. Typical operating flowrates are 30-50 gpm. Electricity costs between $20,000 and $30,000 per year, and total costs for operation are estimated
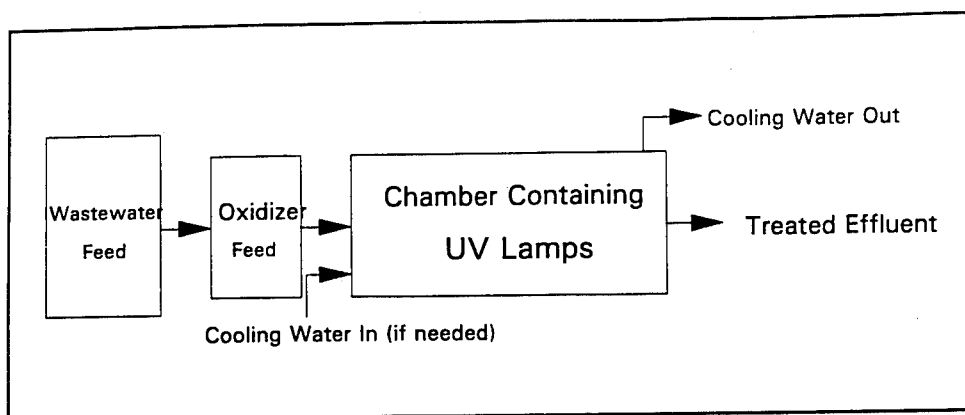
Figure 4.   Schematic diagram of typical UV/ChO system

at approximately $35,000 to $40,000 per year. Costs can vary depending on whether low-pressure or medium-pressure lamps are used and whether ozone or hydrogen peroxide is used.

Historical studies

In unpublished studies, Jack D. Zeff of Ultrox, Inc., indicated reduction of RDX from 28,900 µg/L to 892 µg/L and HMX from 2,210 µg/L to 336 µg/L at a 40-min residence time using Ultrox, Inc., low-pressure lamps and ozone. Similarly, in unpublished studies, Norman Olson of Peroxidation Systems, Inc., reduced RDX concentrations from 150 µg/L to 6 µg/L in 0.25 min using Peroxidation Systems, Inc., medium-pressure lamps and hydrogen peroxide. In experiments conducted by Solarchem (Reed 1990) using 30-kW lamps, TNT was reduced from 125 mg/L to less than 10 µg/L for a cost of approximately $6.00/1,000 gal.

Project Objective

The main objective of the study was to evaluate the potential for using AOPs for reducing RDX to 2.0 µg/L or less in waters from two locations, well 410 and Building 1383. Two locations were selected because well 410 was the contamination source and water from well 410 is treated in Building 1383. Water collected from other Picatinny wells, (e.g., well 430A), is treated in Building 1383. This mixing of source waters may dilute the concentrations of RDX, possibly affecting the UV/ChO efficiency. Either location could be selected for a full-scale treatment unit. Preliminary screening evaluations were conducted to determine whether bench-scale evaluations should be performed. The bench-scale evaluations were conducted to determine whether UV/ChO could treat the water to RDX levels less than 2.0 µg/L and whether UV/ChO technologies should be evaluated on the pilot-scale level. The pilot-scale studies were conducted in order to verify the results of the bench-scale study and to

compare UV/ChO and GAC adsorption field-scale operating costs for treatment of the two groundwaters.

Project Approach

The WES bench- and pilot-scale evaluations of UV/ChO involved the following:

a. Preliminary evaluations of UV/ChO for treatment of the RDX-contaminated waters.

b. Collection of water from two locations, Building 1383 and well 410, at Picatinny Arsenal, the water treatment facility, and shipment of the waters to WES.

c. Bench-scale evaluations of UV/ChO at WES.

d. Pilot-scale evaluations of UV/ChO at two locations, Building 1383 and well 410 at the Picatinny Arsenal.

e. Comparison of GAC adsorption efficiencies and costs to those of UV/ChO for treatment of the RDX contaminated water.

Figure 5 represents a schematic diagram of the bench- and pilot-scale evaluations conducted at WES and the Picatinny Arsenal, respectively.
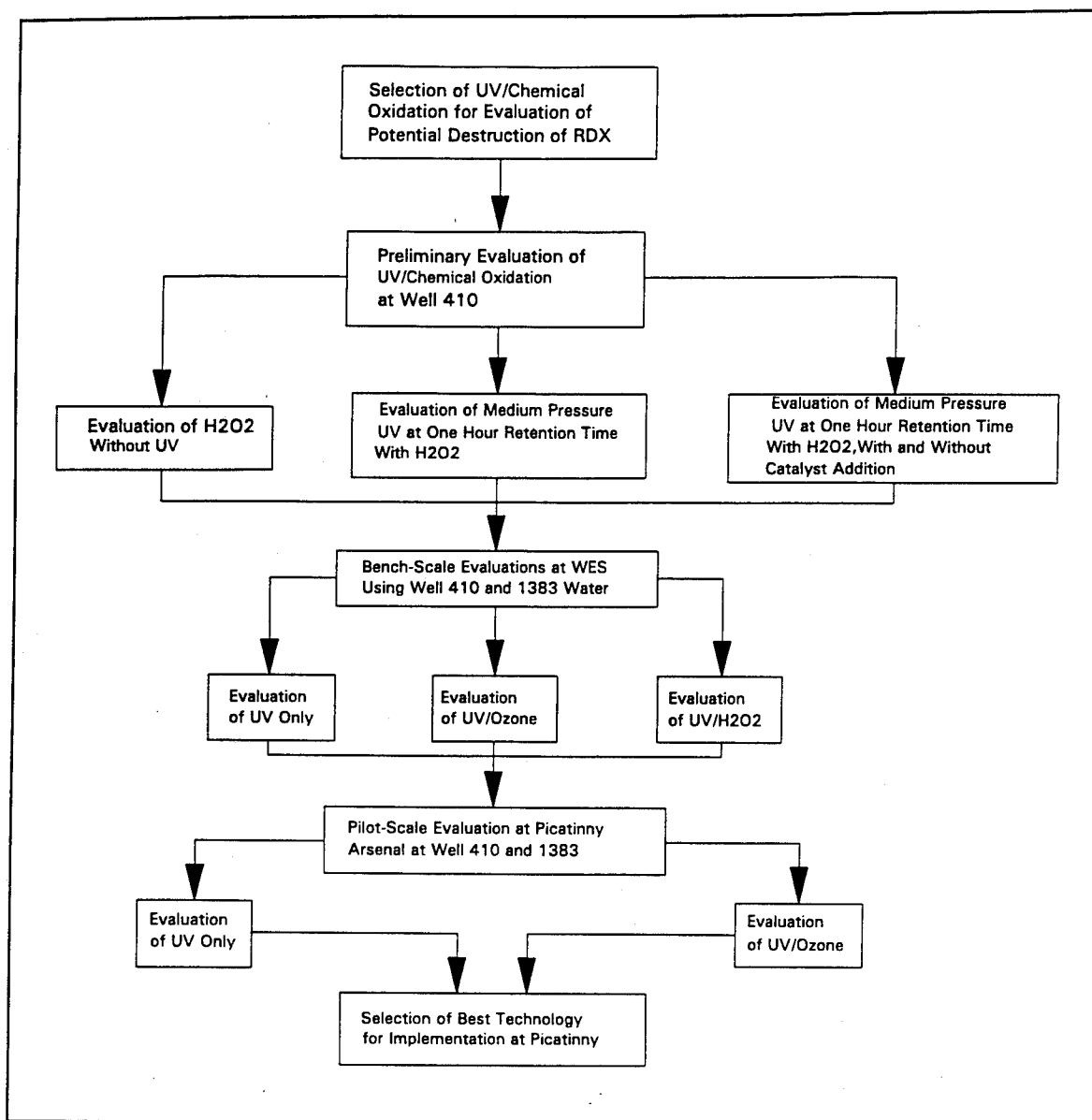
Figure 5.   Schematic diagram of UV/ChO evaluation

2 Bench-Scale Materials and Methods

The preliminary evaluation was conducted at the Picatinny Arsenal using water collected from a spigot at well 410. WES personnel collected groundwater samples for shipment to WES for the bench-scale evaluation. Sample water was collected from well 410 and from the effluent line after the operating green sand filters in Building 1383. Water was obtained from a spigot and pumped directly into 55-gal stainless steel drums. The water was collected and shipped in stainless steel drums to prevent contamination of the water or adsorption of RDX onto the surface of the drum. Approximately 265 gal of groundwater from well 410 and approximately 20 gal of water from the Building 1383 treatment plant were required for the bench-scale evaluation. Both water samples were analyzed to determine the chemical characteristics of the water before UV/ChO treatment. The initial characterization involved determining the iron, chloride, chemical oxygen demand (COD), total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), alkalinity, and turbidity. The characterization results are presented in Table 1 and are discussed in Chapter 3. Upon receipt of the water samples, they were placed in a storage chamber at 4 °C for the duration of the testing program. As water was needed for testing, it was allowed to warm to room temperature before testing began.

For each phase of the bench-scale evaluations and the pilot-scale evaluations, residual hydrogen peroxide was removed to stop oxidation of organics while the sample awaited analysis. Catalase, an enzyme from mammals, was added to decompose the residual hydrogen peroxide and ozone. The approximate molecular weight of catalase is 240,000 g/mole. The catalase used was purchased from Sigma Chemical, catalog no. C-10. All catalases so far isolated contain four tetrahedrally located subunits of equal size. Each subunit consists of a single polypeptide chain which forms proteins (Windholz et al. 1983). In the preliminary screening evaluations, Fisher Scientific EM 10012-1 quant brand strips were used to check for residual oxidizer that might not have been decomposed by the catalase. EM 10012-1 quant strips are 3- by 1/4-in. flexible strips to which are affixed one or more reaction pads that have been sensitized with reagents to react with oxidizers. The test requires insertion of the

14

Table 1
Results of Characterization of Picatinny Waters

Sample Location	Analyte	Replicate	Analyte Conc., mg/L
410	RDX	1	3.2 (µg/L)
		2	3.4
		3	3.6
1,383		1	2.2
410	HMX	1	1.1 (µg/L)
		2	1.3
		3	1.2
1,383		1	0.7
410	Fe	1	0.058
		2	0.038
		3	0.056
1,383		1	0.034
410	COD	1	10.4
		2	8.99
		3	9.01
1,383		1	62.9
410	TOC	1	7.2
		2	6.7
		3	5.0
1,383		1	9.4
410	Alk.	1	69.3
		2	69.2
		3	69.9
1,383		1	104.8
410	Turbidity	1	0.90
		2	0.80
		3	0.80
1,383		1	0.85
410	C1	1	47.0
		2	48.0
		3	48.3
1,383		1	56.0
410	TDS	1	272
		2	240
		3	236

(Continued)

Table 1 (Concluded)			
Sample Location	Analyte	Replicate	Analyte Conc., mg/L
1,383	TDS	1	284
410	TSS	1	8
		2	12
		3	8
1,383		1	2

strip into the sample and color comparison with the provided color scale. In the bench-scale evaluations, quant brand strips and a Hach DR 2000 spectrophotometer were used to determine the completeness of decomposition. The DR 2000 spectrophotometer is a microprocessor-controlled, single-beam instrument suitable for colorimetric testing in the laboratory or the field. Test results can be displayed in percent transmittance, absorbance, or concentration in the appropriate units of measure. Based upon visual analyses of quant brand strips and analytical confirmation using the DR 2000 spectrophotometer, the decomposition reaction was generally completed in approximately 30 min. When no more ozone or hydrogen peroxide was measured, decomposition was considered complete.

Preliminary Screening Evaluation

This phase of study was conducted at the Picatinny Arsenal using water collected from well 410. The water was collected from a spigot which was tapped to the wellhead at 410. The screening evaluation was performed to determine whether UV/ChO treatment should be further considered for bench- and pilot-scale testing.

UV/ChO reactor

A 1-L Ace Glass 7861 reactor was used for the preliminary evaluations. A diagram of the apparatus is illustrated in Figure 6.

Oxidizer

The only oxidizer evaluated was hydrogen peroxide. It was purchased from Fisher Scientific (H325-500) at a 50-percent volume/volume percentage.
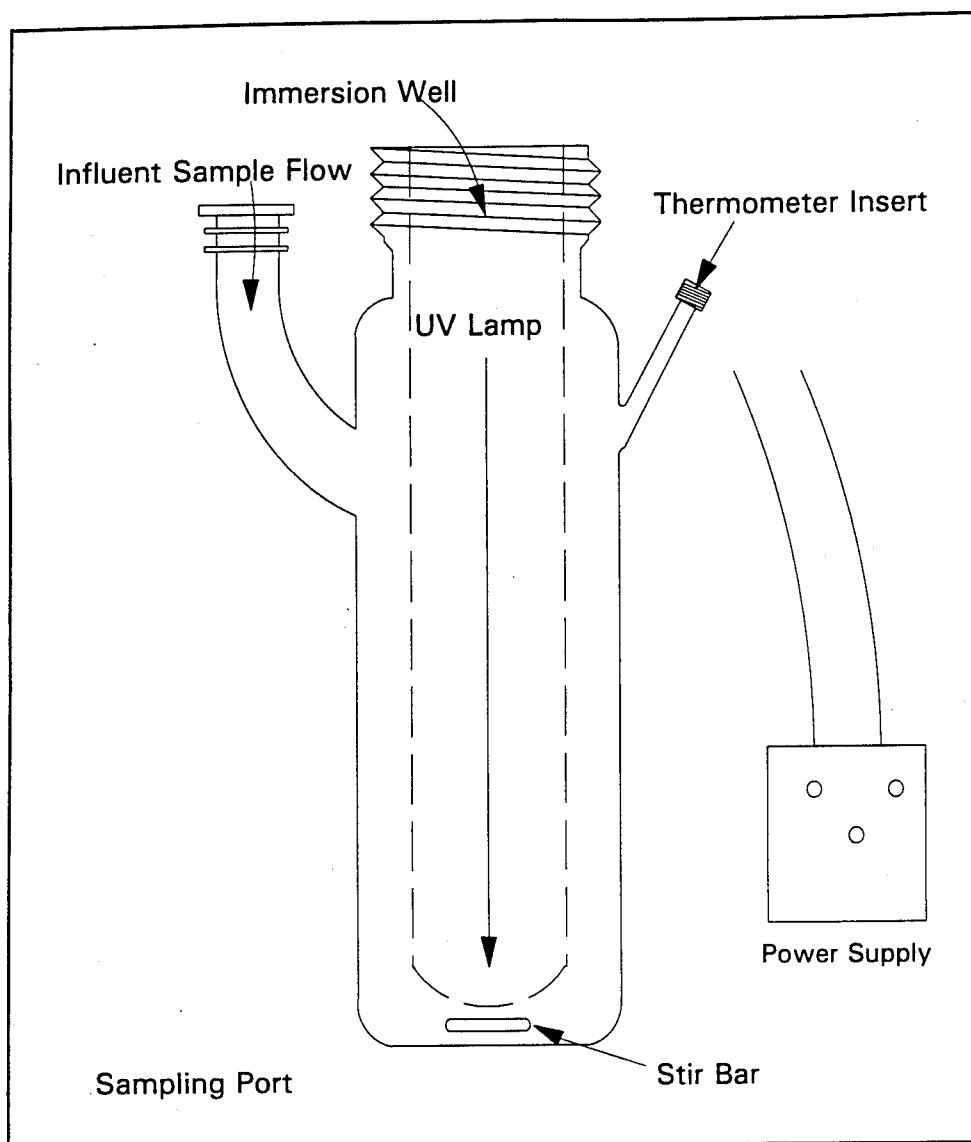
Figure 6.   One-liter reactor used for the preliminary evaluations

Catalysts

Two catalysts, tungsten oxide (WO_3) and UV light, were evaluated. Tungsten oxide was purchased from Fisher Scientific (A325-100). The UV lamps were purchased from Ace Glass (model number 7825) and were medium-pressure 450-W lamps, Ace Glass. Approximately 40-48 percent of the total energy was in the UV portion of the spectrum, 40-43 percent in the visible, and the balance in the infrared.

The purpose of the preliminary screening evaluation was to perform a cost effective evaluation of oxidation of RDX. Four conditions for UV/ChO treatment were studied and are presented in the table below. All photolysis reactions were evaluated at a 1-hr residence time to compare the results. The oxidizer-only evaluation was also conducted using a 1-hr residence time. Ozone was not evaluated because it would have required

Test Condition	Hydrogen Peroxide Conc. mg/L	Tungsten Oxide Conc. mg/L
Oxidizer only	200	0
UV photolysis only	0	0
UV photolysis with hydrogen peroxide	200	0
UV photolysis with hydrogen peroxide and tungsten oxide	200	10

procurement of an ozone generator which was not considered a cost-effective method of screening oxidation technologies at that time.

Bench-Scale Evaluation

UV/ChO reactor

A 3-L Ace Glass 6963 reactor was used for the bench-scale evaluations. A diagram of the apparatus is illustrated in Figure 7.

Oxidizer

Hydrogen peroxide and ozone addition were evaluated. Hydrogen peroxide was purchased from Fisher Scientific at a 50-percent volume/volume percentage. Ozone was generated with an Ozoteq Model 4172 ozone generator and diffused into the Picatinny waters through a Fisher 11139B air stone with an average pore size of 60 μm.

Catalysts

One catalyst, UV light, was evaluated at two intensities. Only one catalyst was evaluated due to the photoreactive properties of UV light; it was determined that addditional catalysis was not required for destruction of RDX. The medium-pressure UV light 450-W lamp (Ace Glass number 7825) was used. The power supply required for the medium-pressure lamp was Ace Glass 7830. Of the total energy radiated, 175.8 W, approximately 40-48 percent was in the UV portion of the spectrum, 40-43 percent in the visible, and the balance in the infrared. A low-pressure lamp (Ace Glass 12128) was also evaluated and had a UV output at a principal wavelength of 254 nm and 3.5 W. Total lamp power consumption was 12 W. The power supply for the low-pressure lamp was Ace Glass 12128-40.
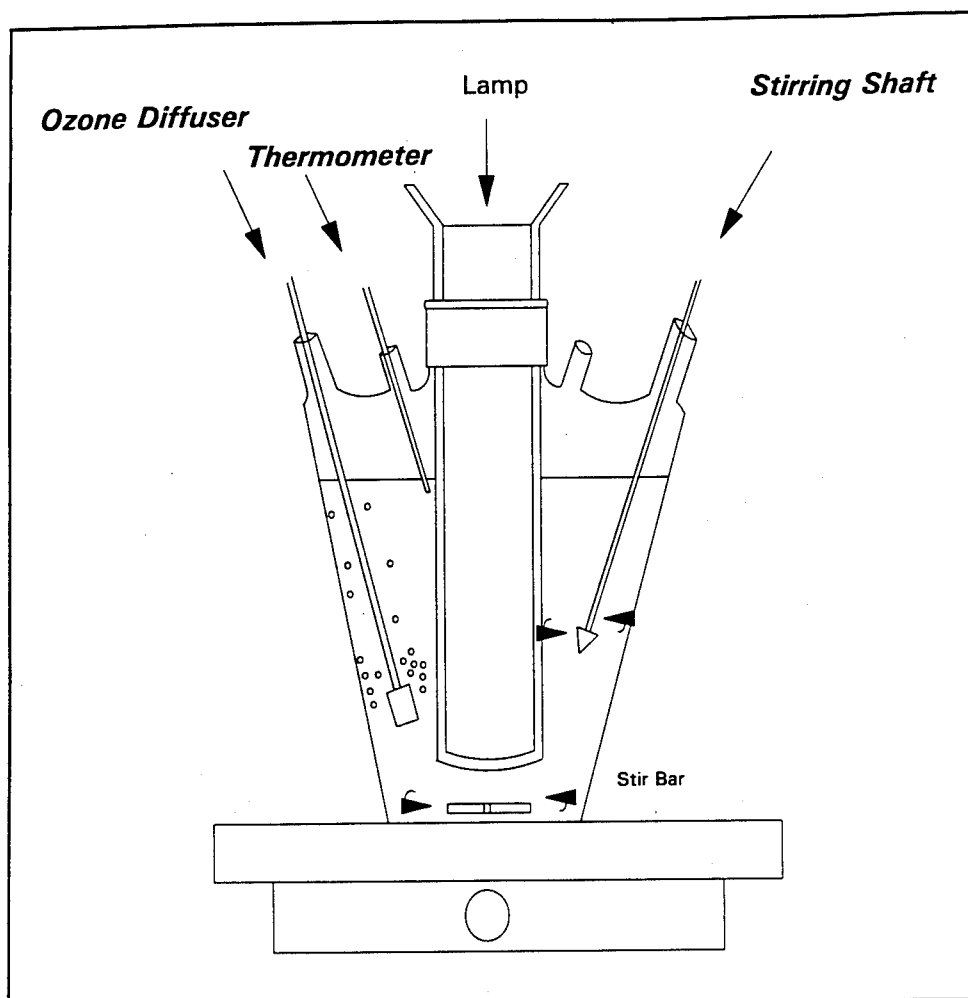
Figure 7.   Three-liter reactor used for the bench-scale evaluation

pH adjustment

Although pH adjustment was referenced as a test parameter in the bench-scale scope of work (Fleming 1992), it was not evaluated due to results obtained without pH adjustment. Without pH adjustment, RDX was destroyed in less than 1 min. Therefore, adjustment of the pH to reduce RDX faster was considered unnecessary.

Treatment Conditions

Three treatment conditions were evaluated in the bench-scale UV/ChO evaluations and are discussed below. Before illumination of lamps or oxidizer addition/generation, the reactor was completely filled using a peristaltic pump and mixing devices were activated. Samples were collected in precleaned bottles and processed according to the appropriate steps shown in Figure 8. Oxidizer addition without photolysis was not evaluated
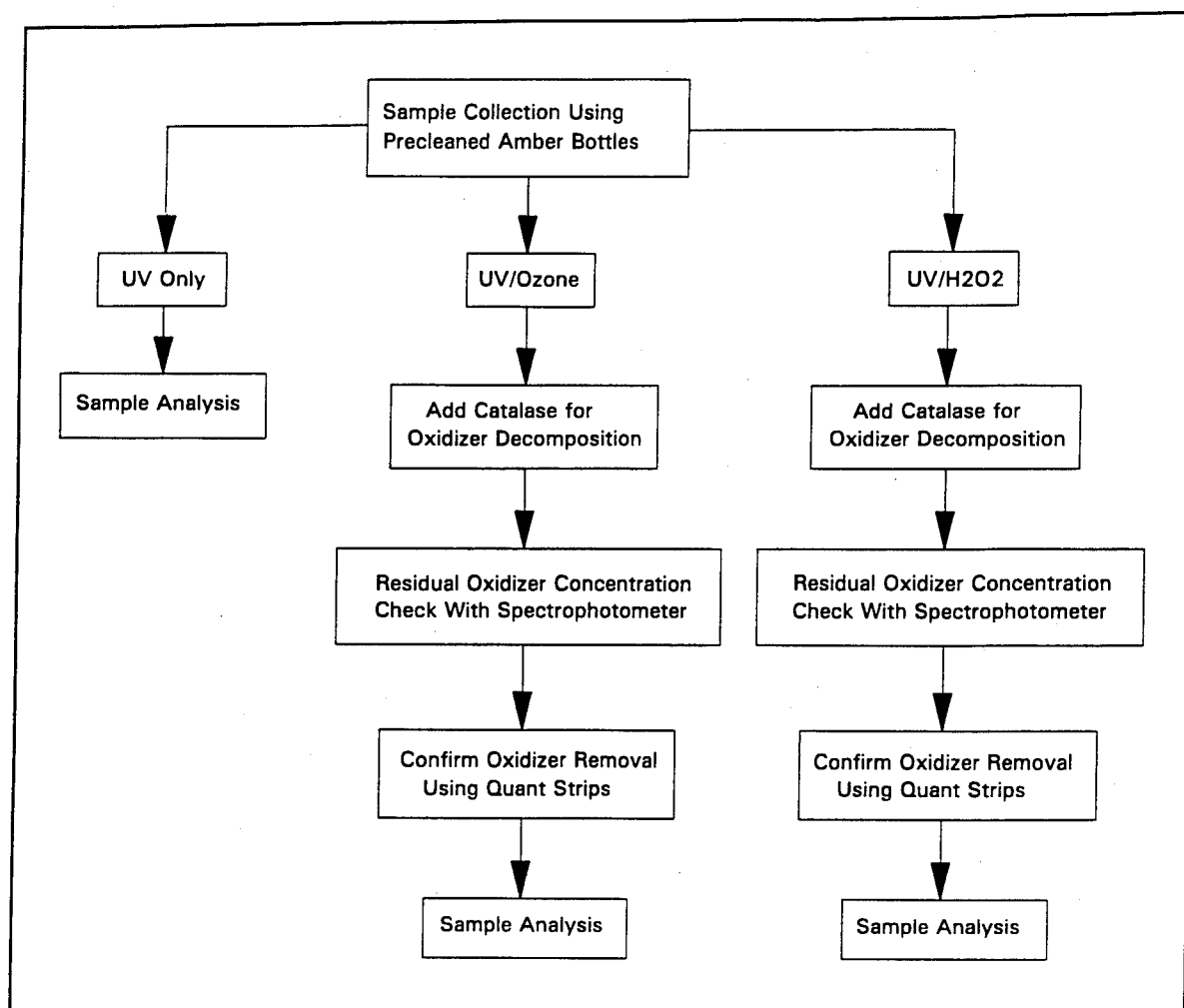
Figure 8.   Diagram of sample collection and handling procedures for bench-scale and pilot-scale studies

based upon pretest results discussed in Chapter 3. Table 2 presents the test conditions for all of the test runs evaluated in the bench-scale study for all test runs.

UV photolysis without an oxidizer

After UV irradiation, the samples were collected in precleaned, 1-L amber bottles at the various residence times listed in Table 2, run nos. 1-2, and 7-46.

UV photolysis with hydrogen peroxide addition

After the reactor was filled and stirring mechanisms activated, a hydrogen peroxide dosage of 250 mg/L was added and the UV light illuminated. The 12-W and 450-W lamps were both evaluated. Samples were collected

Table 2
Test Conditions Evaluated in the Bench-Scale Evaluation

Water Location	Run No.	UV Intensity W	Oxidizer	Residence Time min	RDX Conc. µg/L
410	1	12	None	0	3.2
				30	<0.5
	2	450	None	0	3.2
				30	<0.5
	3	12	Ozone	0	3.2
				30	<0.5
	4	450	Ozone	0	3.2
				30	<0.5
	5	12	H_2O_2	0	3.2
				30	<0.5
	6	450	H_2O_2	0	3.2
*				30	<0.5
410	7-11	12	None	0	3.2
				5, 10, 15, 20, 25	<0.5
	12-16	450	None	0	4.0
				5, 10, 15, 20, 25	<0.5
		12^1	None	0	4.80
	17			1	0.622
	18-21			2, 3, 4, 5	<0.617
	22-26	450^1	None	0	4.77
**				1, 2, 3, 4, 5	<0.617
410		12^1	None	0	3.88
	27			0.25	2.57
	28			0.50	1.90
	29			0.75	<0.617
	30-32	450^1	None	0	4.90
***				0.25, 0.50, 0.75	<0.617
1,383	33-39	450^1	None	0	3.66
				1, 2, 3, 4, 5, 10, 15	<0.617
	40-46	12^1	None	0	3.61
***				1, 2, 3, 4, 5, 10, 15	<0.617

* First round of testing.
** Second round of testing.
*** Third round of testing.
[1] Analysis conducted by ADL. Previous analyses conducted by WES ECB.

in precleaned 1-L amber bottles at the various residence times listed in Table 2, run nos. 5-6.

UV photolysis with ozone addition

Table 2 presents the conditions evaluated using UV photolysis and ozone addition, runs 3-4. The ozone generator was operated 24 hr/day to continue purging the air dryer. Continuous operation of the generator was needed for the desiccant in the dryer to absorb moisture, which affects ozone production. After the reactor was filled and stirring mechanisms activated, the ozone flow was initiated. For maximum ozone dosage, the variable transformer was operated at a high voltage in combination with low air flow, yielding 1.75-percent ozone (wt/wt) in air. Conversely, a low voltage combined with high air flow was used to generate lower ozone concentrations. However, maintaining maximum ozone concentrations is dependent upon ozone decomposition/adsorption within the fluid (see "Chemical Oxidants" in Chapter 1).

RDX analyses

After the residence time was complete, samples were collected in precleaned, 1-L amber bottles. RDX analyses was conducted according to methods described in UW 26 (Miyares and Jenkins 1990), a method demonstrated by ADL for USAEC (ADL 1992). The method analyzes for explosives in water using high-performance liquid chromatography with UV detection.

3 Discussion of Bench-Scale Results

Characterization of Source Water

Characterization of the Picatinny waters was conducted by ECB and the results are presented in Table 1. In many cases, fouling of UV tubes occurs when concentrations of iron are greater than 3 mg/L or alkalinity is more than 500 mg/L (Kreft, Scheible, and Venosa 1986). Transmittance of UV light is inhibited by the presence of TDS and TSS levels exceeding 400 mg/L and 200 mg/L, respectively. The levels of iron, alkalinity, TDS, and TSS were below the cautionary levels at well 410 and Building 1383, indicating that quartz sleeve fouling probably would not occur.

Preliminary Evaluations

These results were encouraging and demonstrated high potential for successfully treating the source water. The initial concentration of RDX was 4.5 µg/L. For the four conditions tested in the preliminary evaluation study, a 1-hr residence time was chosen. Normal operating ranges for UV/ChO are generally 40 min or less. Typical hydrogen peroxide dosages are less than 100 mg/L. However, this test was conducted to determine whether RDX was destroyed at maximum operational conditions, including high oxidant dosage of 200 mg/L and a high residence time of 1 hr. ADL performed the RDX analyses for treated and untreated samples and their detection limit was 0.617 µg/L. The concentrations of RDX in the treated waters were <0.617 µg/L for all conditions involving UV photolysis: UV photolysis alone, UV photolysis with addition of hydrogen peroxide, and UV photolysis with addition of hydrogen peroxide and tungsten oxide. Oxidation alone, without UV photolysis, did not show any signs of destruction of RDX. The initial concentration of RDX was 4.5 µg/L, and the final concentration using hydrogen peroxide only was 4.5 µg/L. Based upon the results of the preliminary testing, the bench-scale evaluations were initiated. Oxidant addition, without UV photolysis, was not evaluated further.

Bench-Scale Evaluation

The approach to the bench-scale evaluation included testing to determine the minimal operating conditions necessary for cost-effective treatment. Minimum conditions included shortest residence time, lowest oxidant dosage, and least power requirements necessary for reduction of RDX to <2.0 µg/L.

Well 410 evaluations

Bench-scale testing was begun using water from well 410 because well 410 RDX concentrations were higher than RDX concentrations in Building 1383 waters (see Table 1). The results obtained for the well 410 water were used to set the test conditions for testing of the Building 1383 water.

Thirty-minute residence times were used at the conditions presented in Table 2, run nos. 1-6, with addition of ozone and hydrogen peroxide, and UV photolysis alone, for both UV intensities. The RDX concentrations for all of the test runs were <0.617 µg/L. Further tests were conducted at residence times less than 30 min.

UV photolysis alone was evaluated using both UV sources. The residence times evaluated were 5, 10, 15, 20, and 25 min. The RDX concentrations for all of the runs, nos. 7-16, were <0.617 µg/L.

UV photolysis without an oxidizer, using both UV sources (run nos. 17-26), was evaluated at residence times of 1, 2, 3, 4, and 5 min. The results of the 2-, 3-, 4-, and 5-min residence times were <0.617 µg/L RDX for both UV intensities. At the 1-min residence time, using the 12-W lamp (run no. 17), the result was 0.622 µg/L RDX, and the result for the 450-W lamp (run no. 22) was <0.617 µg/L RDX. These results indicated that RDX in this water is extremely reactive to UV photolysis and concentrations were lowered to the desired levels in less than 1 min by both UV light sources.

1383 water treatment plant tests

Based on the results of well 410 evaluations, a narrow set of conditions was selected for evaluation of the Building 1383 waters. The residence times tested were 1, 2, 3, 4, 5, 10 and 15 min (run nos. 33-46 in Table 2) using both UV sources without oxidizer input. All RDX concentrations in the treated water were <0.617 µg/L.

24

4 Pilot-Scale Materials and Methods

The pilot-scale study involved evaluation of chemical oxidation at two onsite locations. The first location was at well 410. The second location was at Building 1383. The materials and methods used were the same at both locations, except for the water connections, which will be differentiated between the two locations.

ADL was contracted by WES to assist with the onsite pilot study and to procure the equipment and services of an AOP vendor. Results of the bench-scale study showed that the RDX in source water could be reduced to 0.622 μg/L with a low-pressure UV lamp, no oxidizer, and 1-min residence time. The vendor selected for the pilot-scale evaluation was Ultrox because its system was configured to meet the treatment needs. The system includes low-intensity UV lights, which require less power (Lewis, Topudurti, and Foster 1990) than high-intensity lamps. Figure 9 is a picture of the Ultrox unit taken during operation at the site. The Ultrox system included thirty 65-W lamps, considered to be low-wattage lamps relative to other vendors (e.g., Peroxidation Systems, Inc., lamps are 5 kW and Solarchem lamps are 30 kW). Based on conversations with Ultrox personnel, the concentrations of TDS, TSS, alkalinity, and Fe in the Picatinny waters would not affect UV transmittance or foul the quartz sleeves housing the low-pressure lamps.

Three test conditions were evaluated at each location:

a. UV Photolysis only—no oxidizer addition.

b. UV Photolysis with High Ozone—1.5-percent ozone in the influent air stream.

c. UV Photolysis with Medium Ozone—0.5-percent ozone in the influent air stream.

The primary wavelength of low-pressure mercury lamps such as the ones utilized in the Ultrox system is 254 nm. Ozone adsorption of UV light occurs primarily at 254 nm (Zappi et al. 1992). Hydrogen peroxide
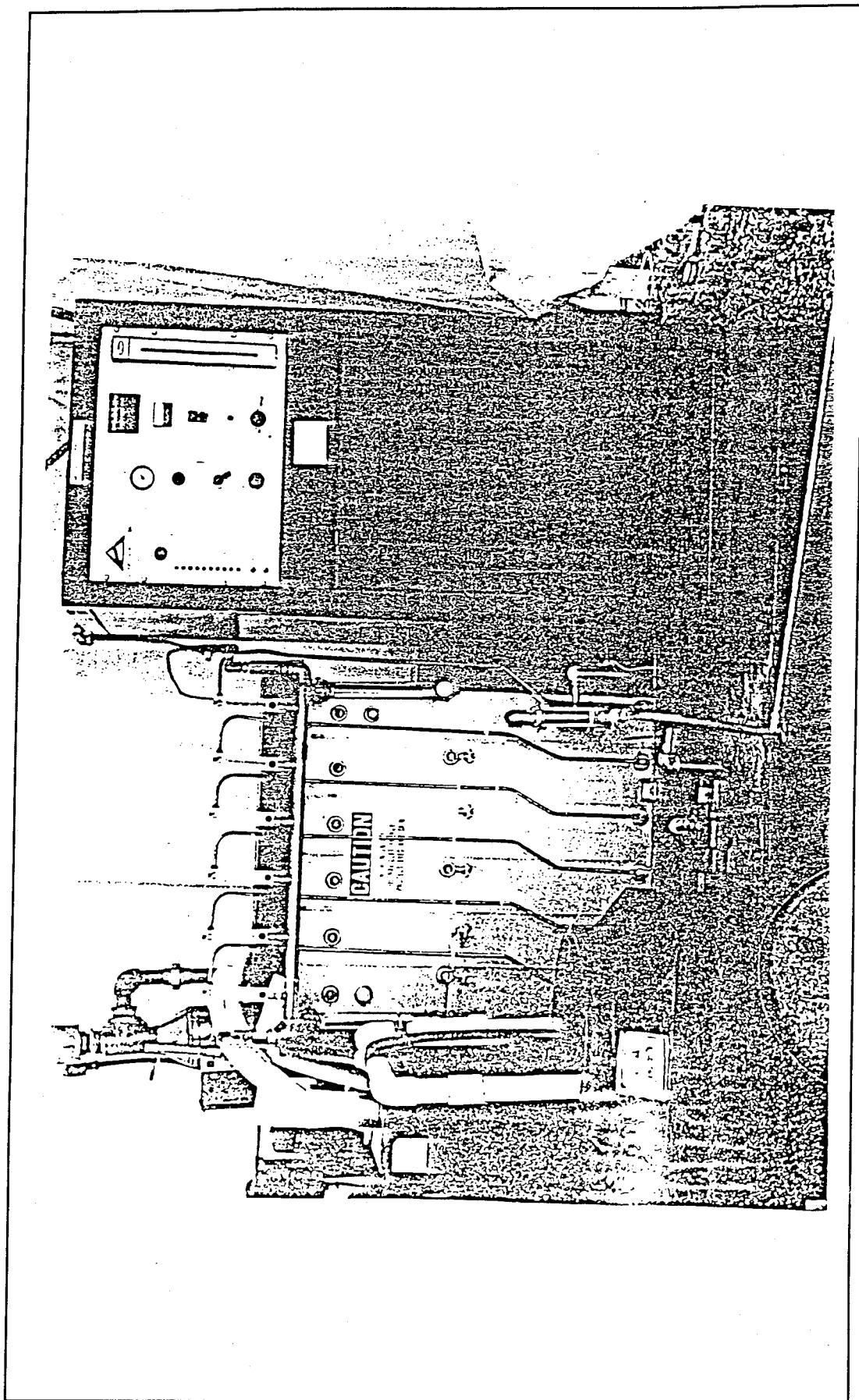
Figure 9. Onsite operation of Ultrox unit at well 410

was not evaluated further because hydrogen peroxide systems have primary adsorption at wavelengths shorter than 254 nm, which is the primary emission of medium-pressure lamps.

For each of the three conditions listed above, triplicate runs were performed at residence times of 3.75, 8.75, 13.75, and 27.5-min and samples collected and submitted for analysis. To obtain the residence times, the UV/ChO unit was operated at two flowrates, 2.5 gpm and 5 gpm. The Ultrox system consists of six chambers. Sampling from the individual chambers results in variation of the residence time. The 3.75-, 8.75-, and 13.75-min residence times were obtained at a flowrate of 5 gpm and were collected from cells 2, 4, and 6, respectively (see Figure 10). The 27.5-min residence time was obtained at a flowrate of 2.5 gpm and was collected from cell 6 (see Figure 10). The high-performance liquid chromatography (HPLC) chromatograms were analyzed to determine the minimum residence time required for the highest reduction of RDX levels for each of the three conditions listed above. Also considered in the analysis of the chromatogram was the formation of intermediates from the chemical oxidation process. Specific intermediate compounds were not identified.
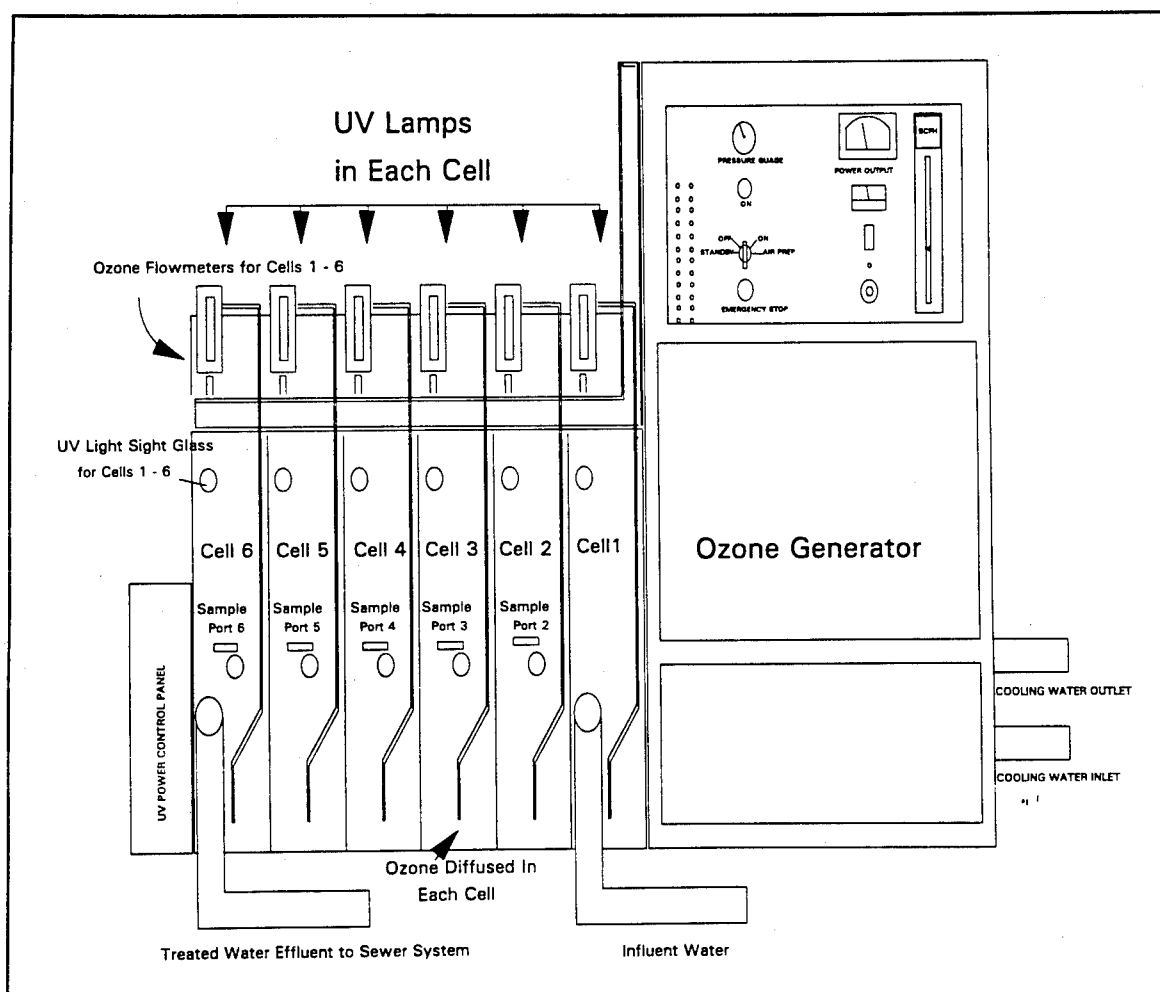
Figure 10. Pilot-scale reactor

Verification runs were performed based on a determination of the most cost-effective conditions (i.e., minimum flowrate and minimum oxidizer concentration at which the most complete destruction of RDX occurred in the initial test run). Also considered was the formation of intermediates shown in chromatographic results. Verification runs included duplicating optimum conditions at either of two flowrates, 2.5 gpm or 5 gpm. Sampling was done through ports 2, 3, 4, 5, and 6, which are illustrated in Figure 10. One flowrate was selected, and all ports were sampled and the waters analyzed to determine whether a gradient of RDX destruction would be observed as residence time increased. At a flowrate of 2.5 gpm, the residence times for reactions cells 2 through 6 were 7.5, 12.5, 17.5, 22.5, and 27.5 min, respectively. At a flowrate of 5 gpm, the respective residence times were 3.75, 6.25, 8.75, 11.25, and 13.75 min.

Water Source

The Ultrox unit was connected to the wellhead at well 410 by 3/4-in. copper tubing. Picatinny Arsenal personnel installed the piping to the unit, which included a brass pressure reducer at the wellhead. Water pressure was reduced from 200 psi to 40 psi before it entered the Ultrox unit. Excessive pressure can cause breakage of the quartz sleeves and the UV lamps. At the water treatment plant, Building 1383, water was supplied to the treatment unit prior to chlorination because chloride anions can contribute to the formation of undesirable intermediates during chemical oxidation of RDX. The water was supplied through copper tubing at a reduced pressure of 40 psi. Cooling water was supplied to the unit through 3/4-in. copper tubing at a flowrate of 4 gpm at both locations.

Influent water was piped to the reactor's cell-1 and treated effluent exited from cell-6 as shown in Figure 10. The reactor was designed for a maximum flowrate of 5 gpm. Because UV lamps emit heat from radiation, the reactor was cooled by circulating chilled water, approximately 60 °F, through jackets in the reactor at a flowrate of 4 gpm.

Power Requirements

Electrical supply was installed at both testing locations by Picatinny Arsenal personnel. The unit required 460-volt, three-phase input voltage, with a circuit breaker rating of 30 amps. Power requirements during actual test runs were determined using a portable power meter. The power requirement measurements were inclusive for the entire unit. Although the unit had published power requirements, a real time measurement was desired to determine onsite operating costs for the UV/ChO unit. Readings were taken from three leads located at the power supply box with an amp meter. The three leads represented power for the ozone generator,

the UV lamps, and the air compressor. The readings were averaged and converted to watts. The power requirement for the unit was determined according to the equations presented below.

Example: Three readings—4.5 amps, 5 amps, and 6 amps

To calculate apparent power (Perry, Chitto, and Kirkpatrick 1963),

$$S = VI \tag{6}$$

where

S = apparent power

V = voltage, volts, for the Ultrox P-70 = 460 V

I = current, amps

To calculate the actual absorbed power (Perry, Chitto, and Kirkpatrick 1963),

$$P = VI \cos \theta \tag{7}$$

where

P = actual absorbed power

θ = phase angle between V and I, previously determined by Ultrox, Inc.

$\cos \theta$ = power factor based on θ = 1.73, dimensionless

$$5.1\,A \times 460\,V \times 1.73 = 4.1\,kW \tag{8}$$

Shelter

A 16- by 16-ft tent was rented for protection of the UV/ChO unit. The tent was transported from well 410 after completion of testing and set up at Building 1383 for that phase of testing.

UV/ChO Reactor

Figure 10 is an illustration of the reactor used for the pilot-scale evaluation. The UV/ChO reactor was a 75-gal tank constructed of 304 stainless steel. The reactor was divided into six cells. Each cell contained five 65-W

UV lamps and had a sampling port for sample collection. Figure 11 illustrates the path of water flow as it entered the first cell and exited the last cell.
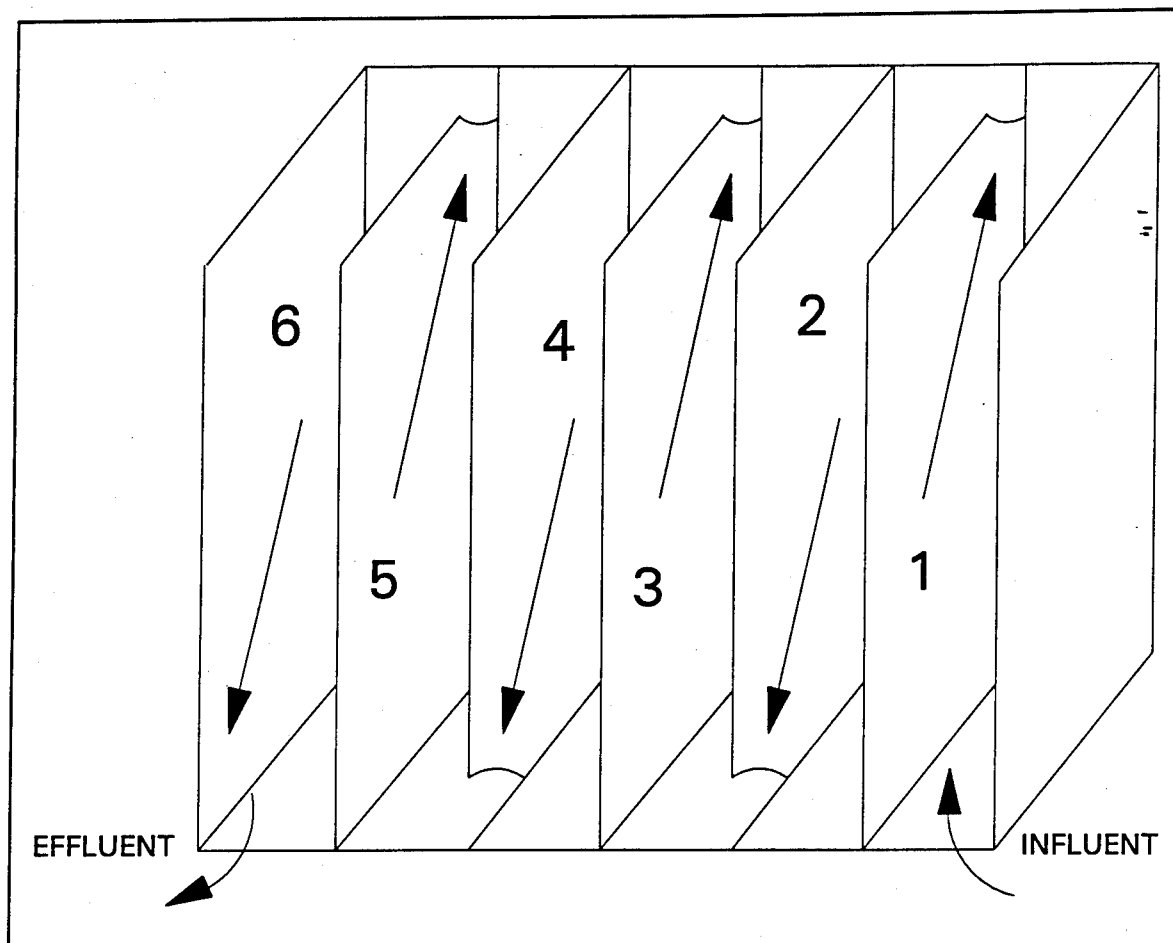
Figure 11. Direction of water flow through cells 1 through 6 in the reactor

Oxidizer Addition

An air compressor supplied air to the ozone generator at 190 standard cu ft/hr. Prior to entering the ozone generator, the air was dried to a -40 °F dewpoint. As air flowed through the ozone generator and through a corona discharge, ozone was generated according to the following equation.

$$O_2 \; (corona \; discharge) \longrightarrow O \cdot + \cdot O \longrightarrow O \cdot + O_2 \longrightarrow O_3 \tag{9}$$
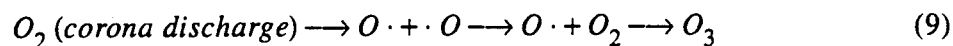
Ozone then flowed through porous ceramic spheres into the 75-gal reactor at the bottom of each cell as shown in Figure 10. Porous ceramic spheres were used to diffuse the ozone into the fluid, allowing maximum surface area contact between the fluid and the gaseous ozonated air. Ozone was

30

added to the reactor at concentrations of 0.5 and 1.5 percent for medium and high ozone dosages, respectively. Ozone concentrations in the air entering the reactor were measured on an ozone monitor connected to the ozone influent line to the reactor. The diffusers were at the base of each cell so that contact was increased as gaseous ozone rose from the base of the cell to the top of the cell.

Ozone decomposition

Ozone causes irritation of the eyes and mucous membranes, pulmonary endema, and chronic respiratory disease. The time-weighted average for ozone is 0.1 ppm. The time-weighted average represents the concentration a worker can be exposed to for a normal 8-hr workday and a 40-hr workweek. The Ultrox ozone generator was capable of producing concentrations above 0.1 ppm. As ozone laden air exited the 75-gal reactor, it flowed through the ozone decomposer. The ozone decomposer contained a nickel catalyst and was heated to 300 °F to decompose ozone. Ambient ozone concentrations were measured by an ozone monitor connected to the effluent line of the ozone decomposer.

Ozone monitors

The ozone system included two monitors, one for ambient air concentrations and the other to measure percent ozone in the air entering the reactor. The ambient air monitor was connected to the effluent of the ozone decomposition unit. The ambient air monitor was equipped with an alarm which sounded if ambient air concentrations exceeded 0.1 ppm. The percent ozone monitor, for measuring percent ozone entering the reactor, was connected to the effluent of the ozone generator, just prior to entrance to the reactor.

Sample Collection

Samples were collected in 1-L, precleaned, amber bottles with teflon-coated lids and residual oxidizer removed according to previously described methods. Samples were shipped in coolers containing blue ice.

Samples were collected and shipped daily or placed in cold storage overnight. Samples were shipped under chain-of-custody to ADL laboratories by overnight delivery.

Sample Analysis

Samples were analyzed for RDX at ADL laboratories using high-pressure liquid chromatography (HPLC) with UV detection, described in UW 26 (ADL 1992) for explosives in water.

5   Discussion of Pilot-Scale Results

Well 410 Results

The results of well 410 testing are presented in Table 3 and discussed below.

UV photolysis without ozone

The runs performed using UV photolysis without ozone are presented in Table 3, run nos. 1-6. The average concentration of RDX in influent waters for three replicates was 4.67 µg/L. The concentration of RDX in the treated effluent for all residence times was <0.617 µg/L. Analysis of the resultant HPLC chromatograms showed formation of chemical intermediates from the oxidation process. However, whether or not the intermediates were formed from the chemical oxidation of RDX was beyond the scope of this study. Figure 12 is an example of an HPLC chromatogram of a sample treated at a residence time of 3.75 min. During RDX analysis, the residence time of RDX in the HPLC column was 3.90 min.

One large peak is present on the chromatogram at a 1.5- to 2-min residence time. The results of peak area determinations are presented in Table A1 of Appendix A. The peak area is an average of 139,599 area units at the 27.5-min residence time, which is lower than the average peak area at the 3.75-min residence time, 283,491 area units. This peak is also present on influent chromatograms (See Figure 13) and in the carbon-treated effluent from the GAC study (Bricka and Fleming, in preparation). In an attempt to identify the peak, two influent water samples were analyzed using Environmental Protection Agency Test Method 625 gas chromatography/mass spectrometry, but all analytes measured were below detection limits for that method. The inability to find highly polar organic compounds by this method suggests the identified peak may represent a highly polar organic. It was beyond the scope of this study to determine the composition of intermediate peaks or any others present. Therefore, whether or not this peak represents a hazardous constituent cannot be determined.

Table 3
Test Conditions Evaluated in the Pilot-Scale Evaluation

Water Location	Run No.	Water Flowrate gpm	Ozone (Conc.)	Residence Time, min	RDX Conc., µg/L
410	1	5	None	0	4.65
				3.75, 8.75, 13.75	<0.617
	2	5	None	0	4.67
				3.75, 8.75, 13.75	<0.617
	3	5	None	0	4.7
				3.75, 8.75, 13.75	<0.617
410	4	2.5	None	27.5	<0.617
	5	2.5	None	27.5	<0.617
	6	2.5	None	27.5	<0.617
410	7	5	0.5%	0	4.66
				3.75, 8.75, 13.75	<0.617
	8	5	0.5%	0	4.58
				3.75, 8.75, 13.75	<0.617
	9	5	0.5%	0	4.72
				3.75, 8.75, 13.75	<0.617
410	10	2.5	0.5%	27.5	<0.617
	11	2.5	0.5%	27.5	<0.617
	12	2.5	0.5%	27.5	<0.617
410	13	5	1.5%	0	4.67
				3.75, 8.75, 13.75	<0.617
	14	5	1.5%	0	4.62
				3.75, 8.75, 13.75	<0.617
	15	5	1.5%	0	4.71
				3.75, 8.75, 13.75	<0.617
410	16	2.5	1.5%	27.5	<0.617
	17	2.5	1.5%	27.5	<0.617
	18	2.5	1.5%	27.5	<0.617
Verification Runs					
410	19	5	0.5%	0	4.82
				3.75, 6.25, 8.75, 11.25, 13.75	<0.617

(Continued)

Table 3 (Concluded)

Water Location	Run No.	Water Flowrate gpm	Ozone (Conc.)	Residence Time, min	RDX Conc., μg/L
1383	20	5	None	0	4.17
				3.75, 8.75, 13.75	<0.617
	21	5	None	0	4.23
				3.75, 8.75, 13.75	<0.617
	22	5	None	0	4.11
				3.75, 8.75, 13.75	<0.617
1383	23	2.5	None	27.5	<0.617
	24	2.5	None	27.5	<0.617
	25	2.5	None	27.5	<0.617
1383	26	5	0.5%	0	4.06
				3.75, 8.75, 13.75	<0.617
	27	5	0.5%	0	4.03
				3.75, 8.75, 13.75	<0.617
	28	5	0.5%	0	4.13
				3.75, 8.75, 13.75	<0.617
1383	29	2.5	0.5%	27.5	<0.617
	30	2.5	0.5%	27.5	<0.617
	31	2.5	0.5%	27.5	<0.617
1383	32	5	1.5%	0	4.31
				3.75, 8.75, 13.75	<0.617
	33	5	1.5%	0	4.28
				3.75, 8.75, 13.75	<0.617
	34	5	1.5%	0	4.16
				3.75, 8.75, 13.75	<0.617
1383	35	2.5	1.5%	27.5	<0.617
	36	2.5	1.5%	27.5	<0.617
	37	2.5	1.5%	27.5	<0.617
Verification Runs					
1383	38	5	0.5%	0	4.43
				3.75, 6.25, 8.75, 11.25, 13.75	<0.617

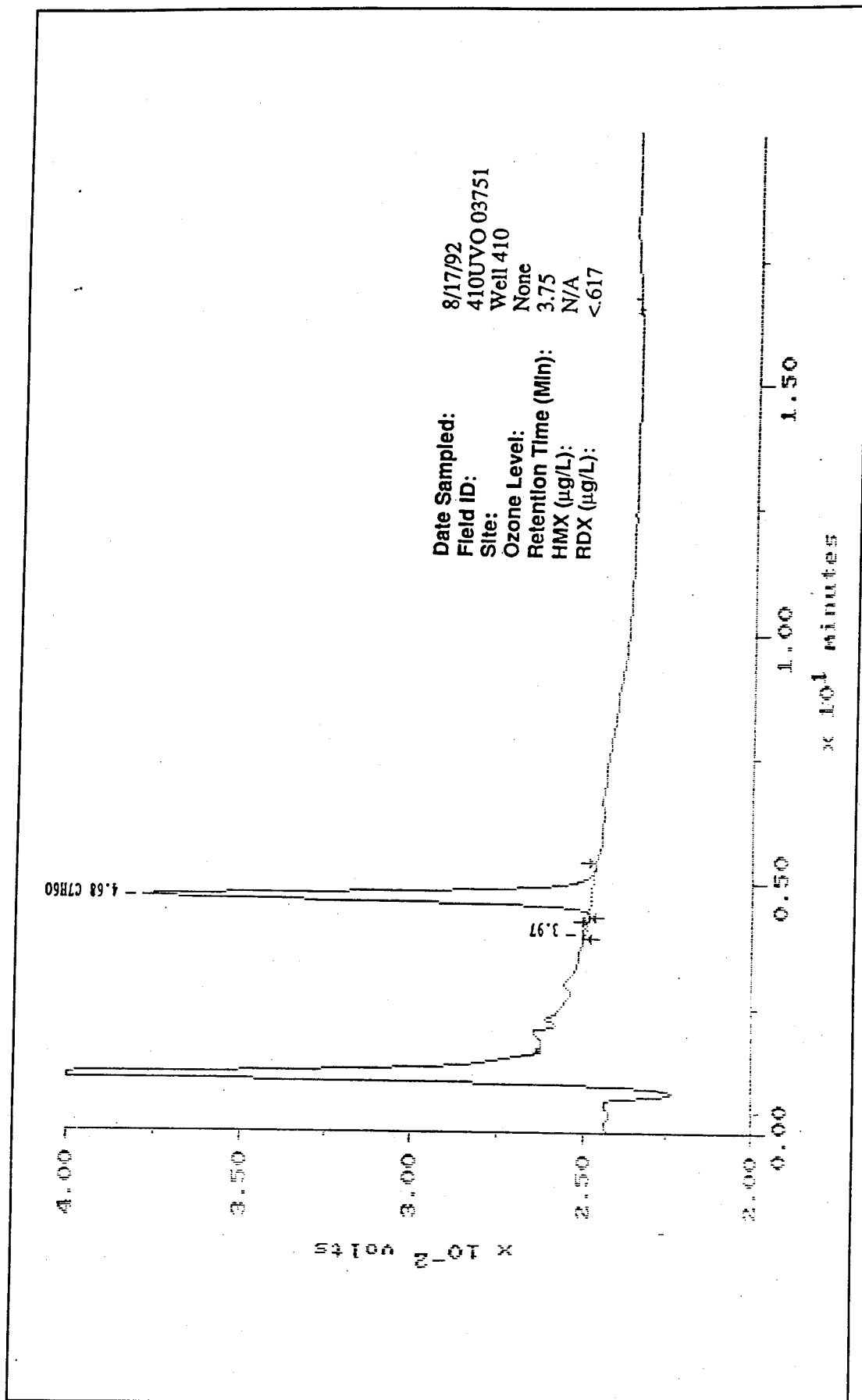| Date Sampled: | 8/17/92 |
Field ID:	410UVO 03751
Site:	Well 410
Ozone Level:	None
Retention Time (Min):	3.75
HMX (µg/L):	N/A
RDX (µg/L):	<.617

Figure 12. Chromatogram for well 410 water treated by UV photolysis alone at a 3.75-min residence time
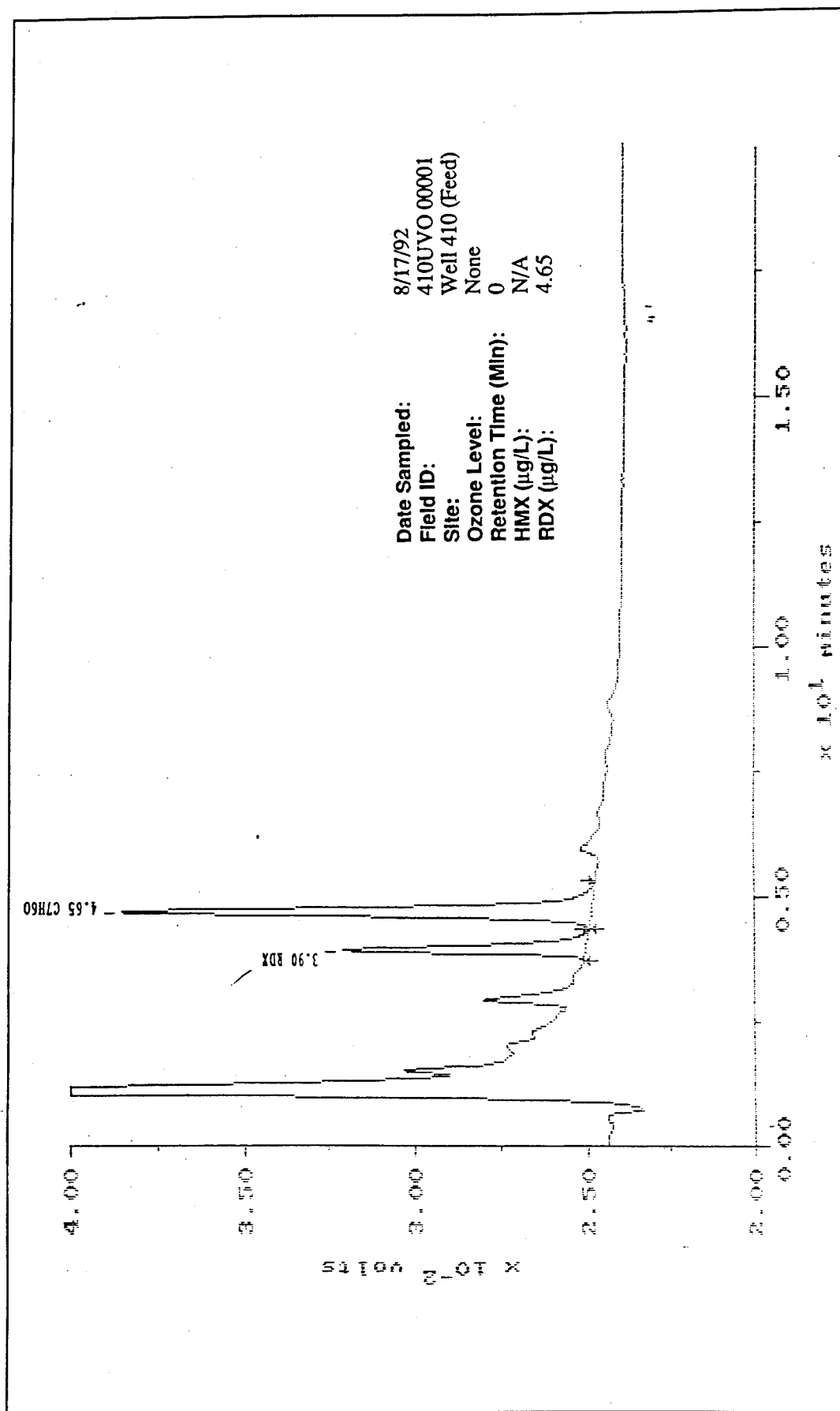
Figure 13. Chromatogram for well 410 influent

However, UV/ChO treatment shows destruction of the peak as residence time increases from 3.75 min to 27.5 min.

UV photolysis with 0.5-percent ozone

The runs performed are presented in Table 3, run nos. 7-12. The average influent water concentration for the three replicates was 4.65 µg/L RDX. The concentration of RDX in the treated water for all residence times was <0.617 µg/L. An example chromatogram from HPLC analysis of the ozone treated samples is presented as Figure 14. This chromatogram shows a reduced peak area for the large unknown peak described in the previous paragraph compared to the chromatograms of untreated waters and waters treated with UV photolysis alone. The average peak area for the 3.75-min residence time with 0.5-percent ozone was 40,263 area units, approximately 14 percent of the peak area at a 3.75 min residence, 283,491 area units, using UV photolysis alone. These data provided the basis for selection of UV photolysis with 0.5-percent ozone for the verification runs.

UV photolysis with 1.5-percent ozone

The runs performed using UV photolysis with 1.5-percent ozone are presented in Table 3, run nos. 13-18. The average influent water concentration was 4.67 µg/L. The concentration of RDX in the treated water for all residence times was <0.617 µg/L. An example chromatogram from HPLC analysis of the ozone treated samples is presented in Figure 15. This chromatogram shows a reduced peak area for the large unknown peak described earlier compared to the chromatograms of untreated waters and waters treated with UV photolysis alone. The average peak area for the 3.75-min residence time with 1.5-percent ozone was 41,493 area units, approximately one-fifth of the peak area at a 3.75-min residence, 283,491 area units, using UV photolysis alone.

1383 Water Treatment Plant Results

The results of water treatment at Building 1383 are presented in Table 3, run nos. 20-38, and discussed below.

UV photolysis without ozone

The runs performed using UV photolysis without ozone are presented in Table 3, run nos. 20-25. The average influent water concentration was 4.17 µg/L RDX. The concentration of RDX in the treated water for all residence times was <0.617 µg/L. The minimum residence time for destruction of RDX to 2.0 µg/L was not determined. The treatment unit was

38
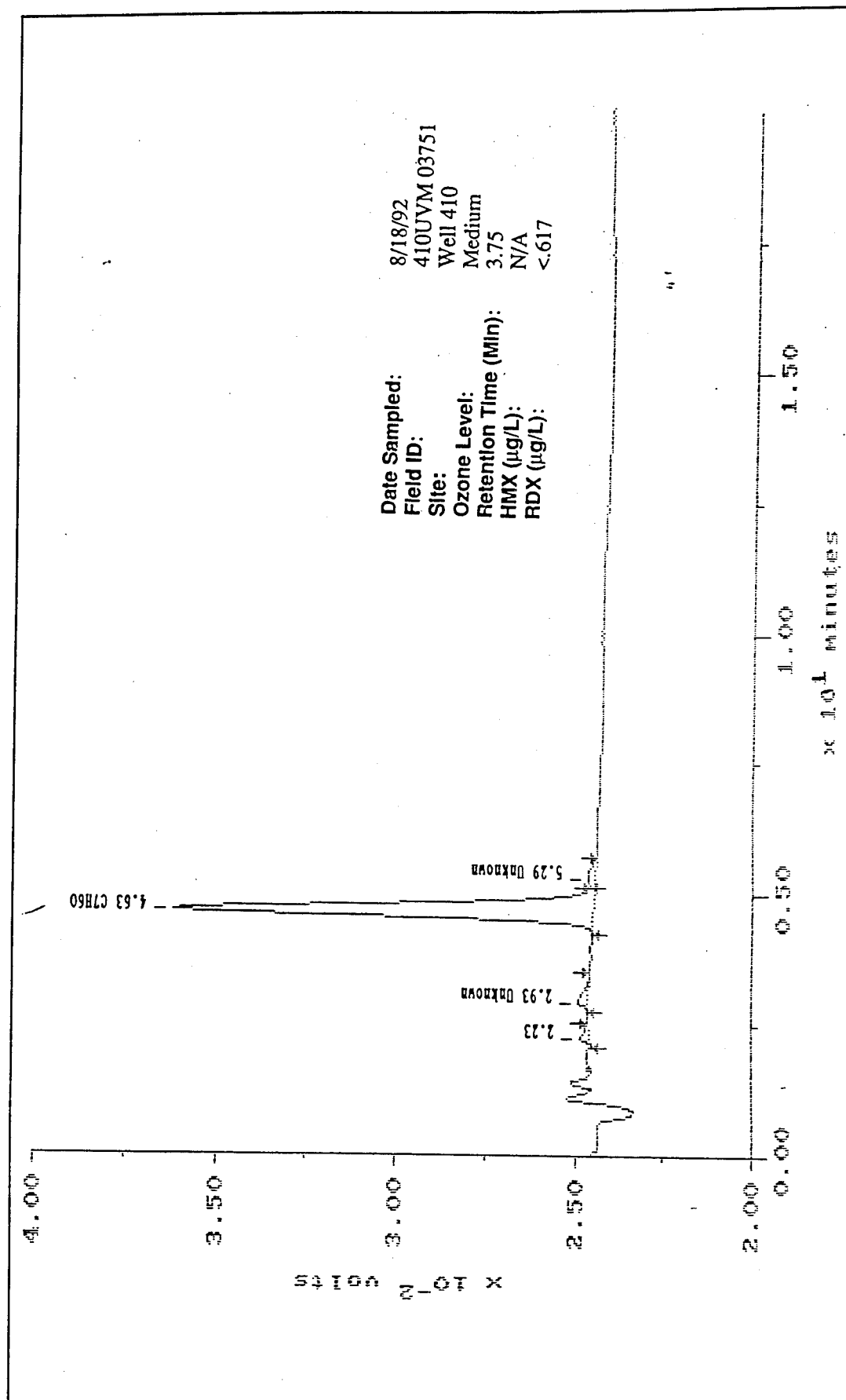
Figure 14. Chromatogram for well 410 treated with 0.5 percent ozone

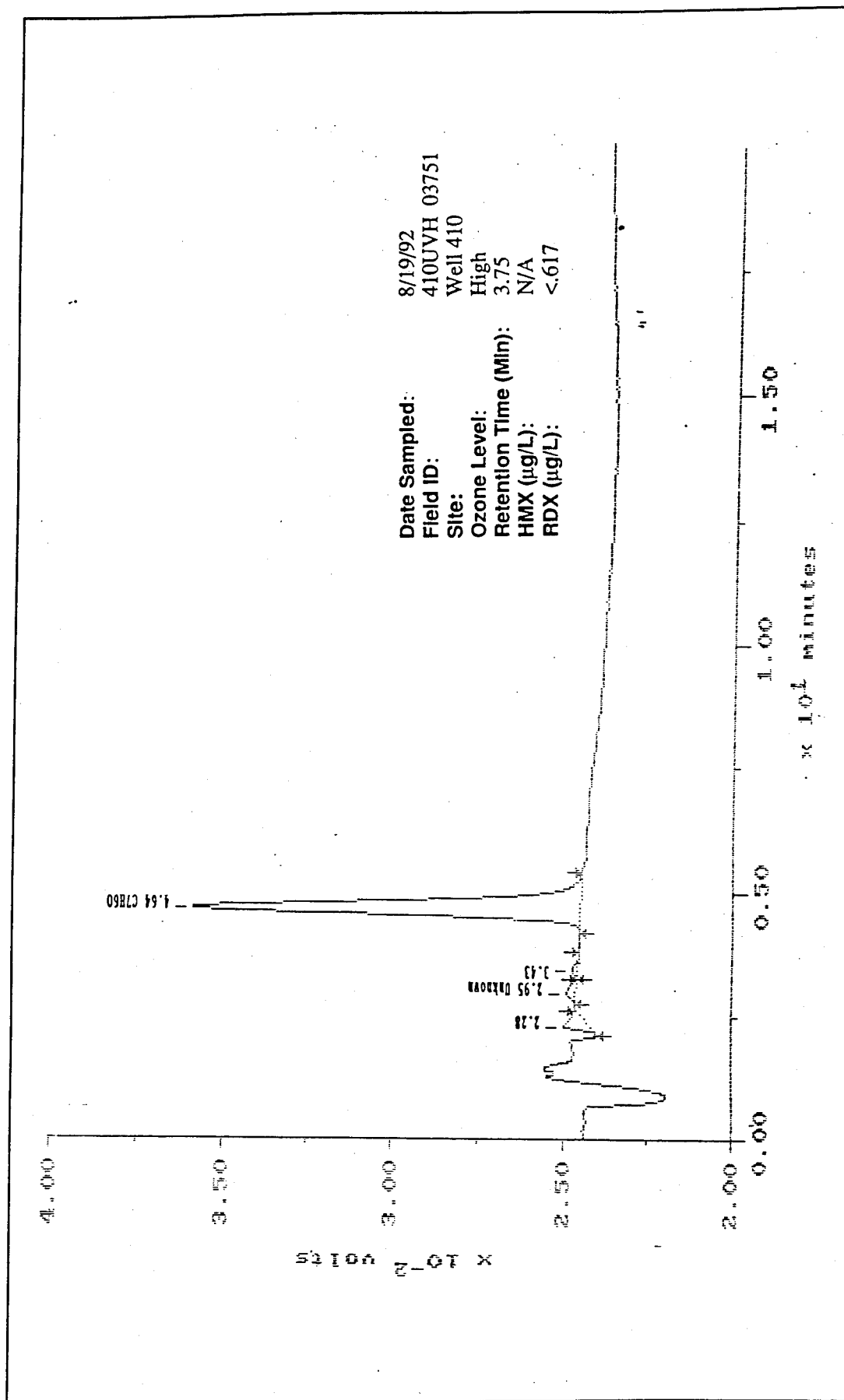| Date Sampled: | 8/19/92 |
Field ID:	410UVH 03751
Site:	Well 410
Ozone Level:	High
Retention Time (Min):	3.75
HMX (µg/L):	N/A
RDX (µg/L):	<.617

Figure 15. Chromatogram for well 410 treated with 1.5 percent ozone

operated at the lowest residence time possible based on its operational capabilities, 3.75 min, and RDX was destroyed to less <0.617 mg/L. Analysis of the resultant HPLC chromatograms showed potential for intermediate formation. Figure 16 is a HPLC chromatogram of the sample treated at a residence time of 3.75 min. During RDX analysis, the residence time of RDX in the HPLC column is 3.90 min. As in well 410 chromatograms, one large peak was present on the chromatogram at a 1.5- to 2.0-min residence time. The results of peak area determinations for the large unknown peak are presented in Appendix A, in Table A1. Though the peak area was reduced, the peak is present at the 27.5-min reactor residence time (see Figure 17). This peak is also present on influent chromatograms (see Figure 18) and in the carbon-treated effluent from the GAC study (Bricka and Fleming, in preparation). As stated previously, while attempts were made to identify the unknown peak, it was beyond the scope of this study to determine the composition of that peak.

UV photolysis with 0.5-percent ozone

Run nos. 26-31 represent the runs performed testing UV photolysis with 0.5-percent ozone. The average influent water concentration was 4.07 µg/L RDX. The concentration of RDX for all residence times was <0.617 µg/L. An example chromatogram from HPLC analysis of the ozone treated samples is presented in Figure 19. This chromatogram shows a reduced peak area for the large unknown peak compared to the chromatograms of untreated waters and waters treated with UV photolysis alone. The average peak area for the unknown, 49,644 area units, compared to the average peak area using UV photolysis alone, 182,077 area units, was 73 percent smaller due to the addition of ozone to the system. These data provided the basis for selection of UV photolysis with 0.5-percent ozone for the verification runs.

UV photolysis with 1.5-percent ozone

Run nos. 32-37 represent the runs performed using UV photolysis with 1.5-percent ozone. The average influent water concentration was 4.25 µg/L RDX. The concentration of RDX in the treated water for all residence times was <0.617 µg/L RDX. An example chromatogram from HPLC analysis of the ozone-treated samples is presented in Figure 20. This chromatogram shows a reduced peak area for the large unknown peak compared to the chromatograms of untreated waters and waters treated with UV photolysis alone, but the reduction is not much less than the 0.5-percent ozone treatment. Further testing would be required to determine the minimum ozone concentration necessary for reducing the area of the large unknown peak.

Figure 16. Chromatogram for 1383 water treatment facility water treated with UV photolysis alone

Figure 17. Chromatogram for 1383 water treatment facility water treated with UV photolysis alone at a 27.5-min retention time

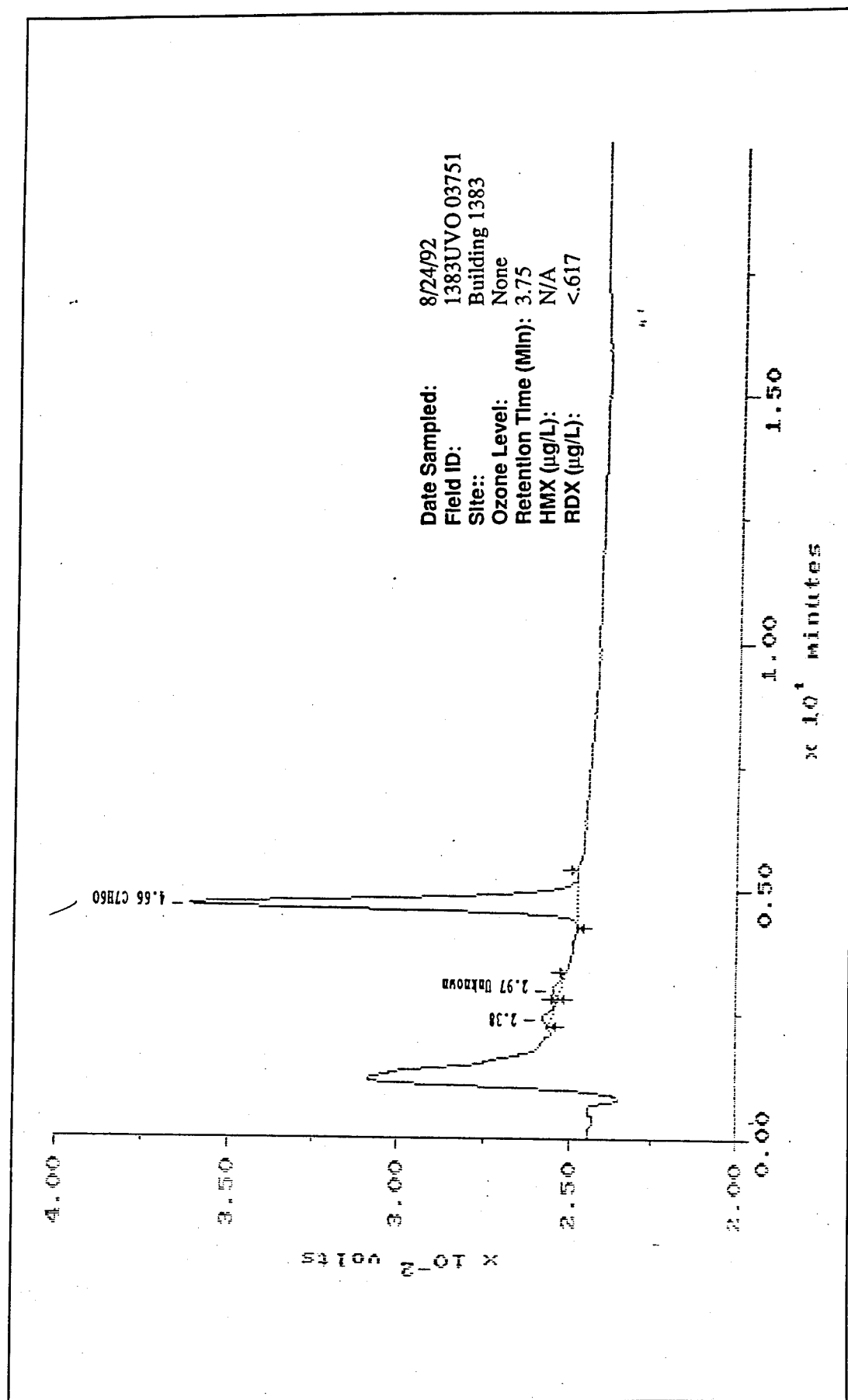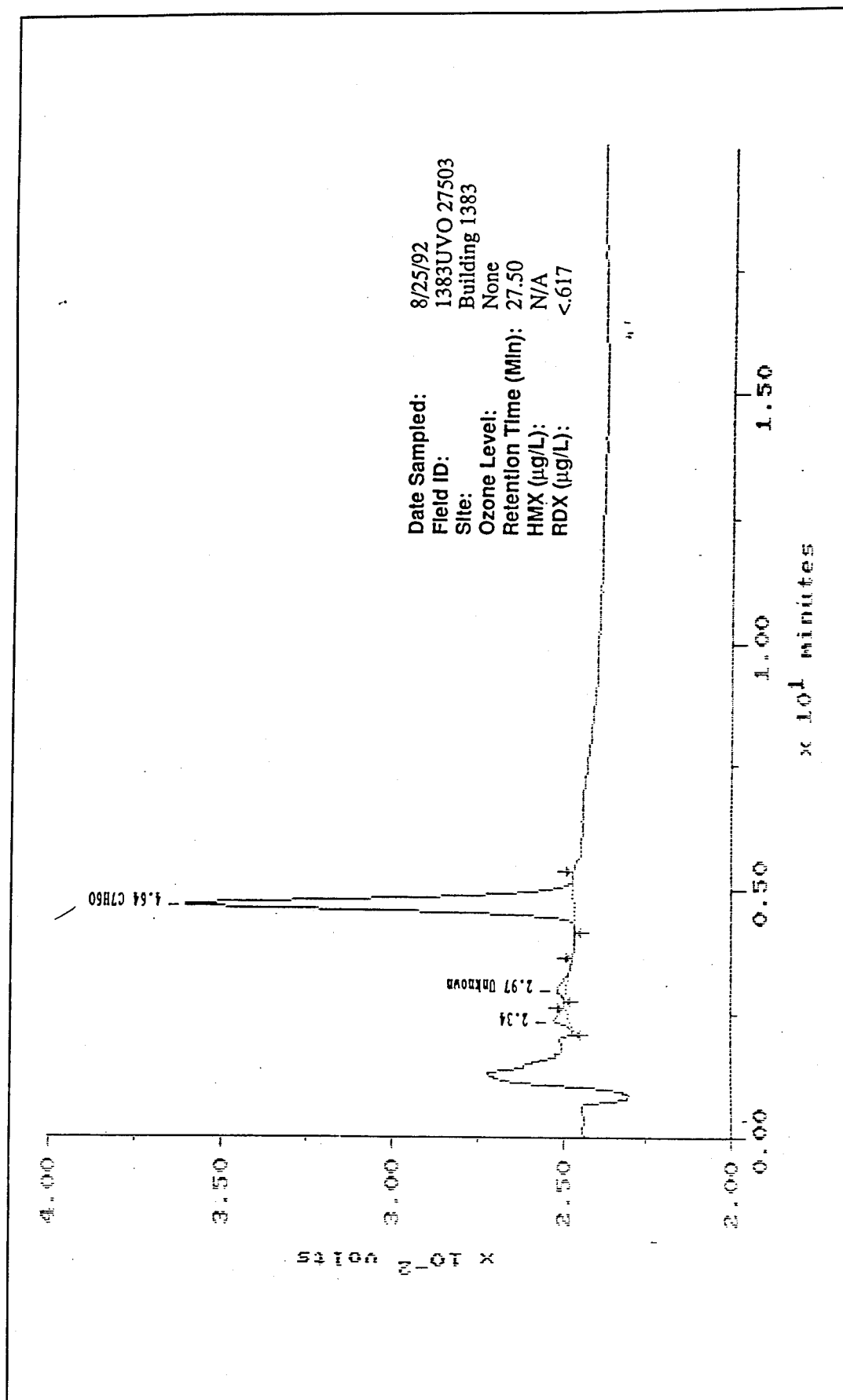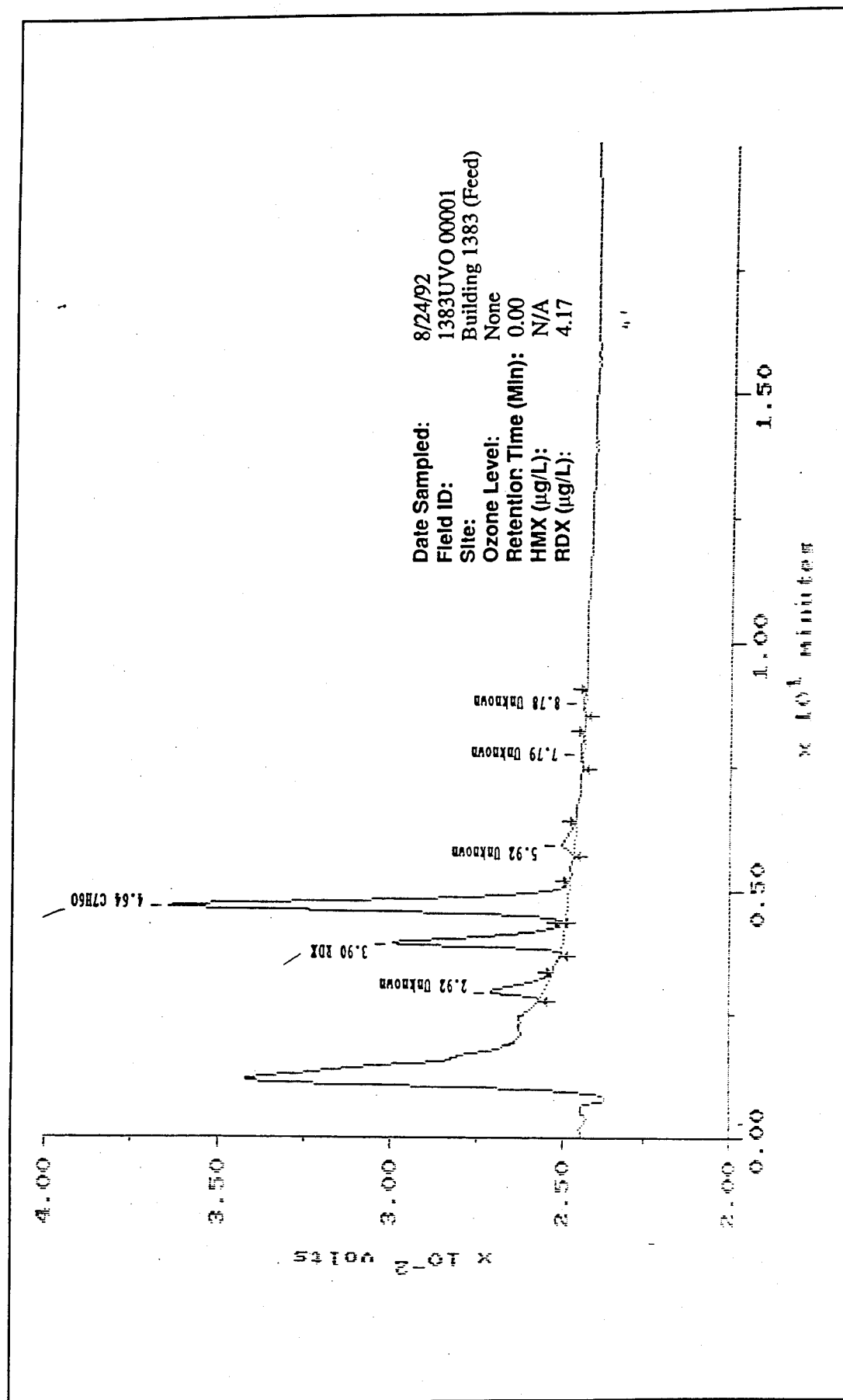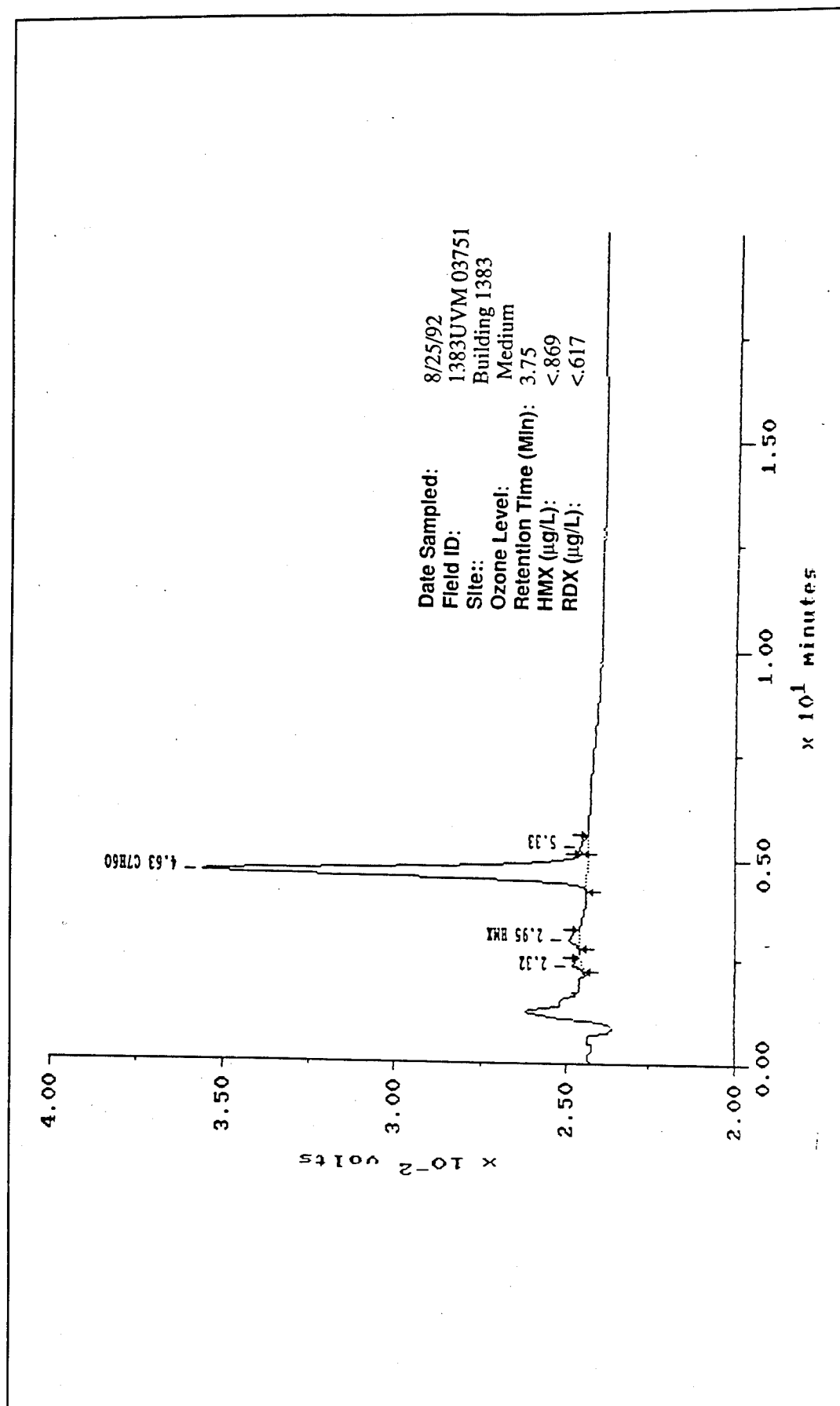Figure 18. Chromatogram for 1383 water treatment facility influent

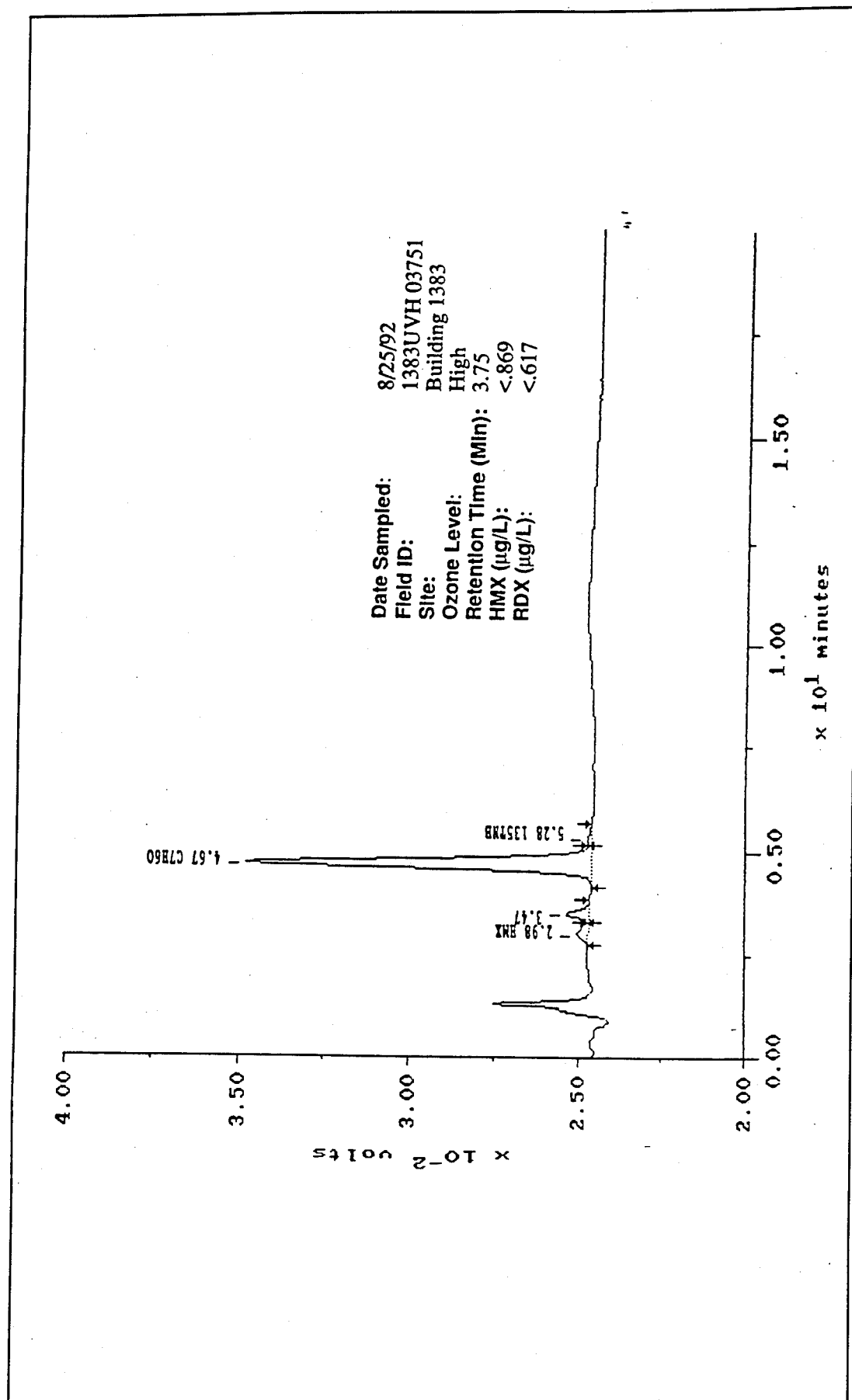Figure 19. Chromatogram for 1383 water treatment facility, water treated with 0.5 percent ozone

Figure 20. Chromatogram for 1383 water treatment facility, water treated with 1.5 percent ozone

Verification Runs

Based upon the results of the first round of pilot-scale testing, one condition, representing optimum treatment, was selected to be used for verification of the initial testing results. The verification run consisted of operating at one flowrate and sampling each cell. This sampling scheme was developed to obtain a gradient of gradual degradation of the RDX.

Well 410 verification runs

A flowrate of 5 gpm with UV photolysis and 0.5-percent ozone addition, run no. 19, was selected for verification because these conditions reduced the area of the large unknown peak the most effectively. The results of peak area determinations for the large unknown peak present in the verification runs are presented in Appendix A, in Table A2. The peak areas determined in the verification runs for the unknown peak described earlier are comparable to the areas determined in the testing runs. The results of the pilot-scale verification run were <0.617 µg/L of RDX in the treated water.

1383 water treatment verification runs

In a similar manner described for well 410 verification runs, a flowrate of 5 gpm with UV photolysis and 0.5-percent ozone addition, run no. 38, was selected for verification because these conditions reduced the peak area of the large unknown peak described previously. The results of peak area determinations for the large unknown peak present in the verification runs are presented in Appendix A, in Table A2. The peak areas determined in the verification runs for the unknown peak are comparable to the areas determined in the testing runs. The results of the verification run were <0.617 µg/L of RDX in the treated water.

Power Consumption

Power requirements were determined for each of the operating conditions evaluated. Power costs for the operation of a field-scale unit could then be calculated. Power meter measurements are presented in Table 4. During the ozone runs, power measurements were taken when the air compressor was on and off. Power measurements were also made at the maximum possible ozone concentration for the unit, 2.2-percent ozone. Figure 21 represents power consumption versus reactor residence time for 0-, 0.5-, 1.5-, and 2.2-percent ozone. There is a small increase in power consumption between 0.5-percent ozone and 1.5-percent ozone, but the HPLC chromatograms do not show increased destruction of RDX or other unknowns by increased ozone concentrations. However, power consumption

Table 4
Results of Power Meter Measurements During UV Photolysis with and without Ozone Addition

Ozone Generation, %	Replicate	Power, kW
0.0	1	2.50
	2	3.55
	3	2.41
	4	2.41
0.5	1	8.65
	2	7.32
	3	8.17
	4	6.10
1.5	1	8.02
	2	7.03
	3	7.06
	4	7.11
	5	9.40
2.2	1	12.07
	2	8.88

is increased from 20 kWhr/1,000 gal using UV photolysis alone to approximately 50 kWhr/1,000 gal using UV photolysis with 0.5-percent ozone, a 30 kWhr/1,000 gal increase in power requirements. Increased power requirements result in increased operational costs.
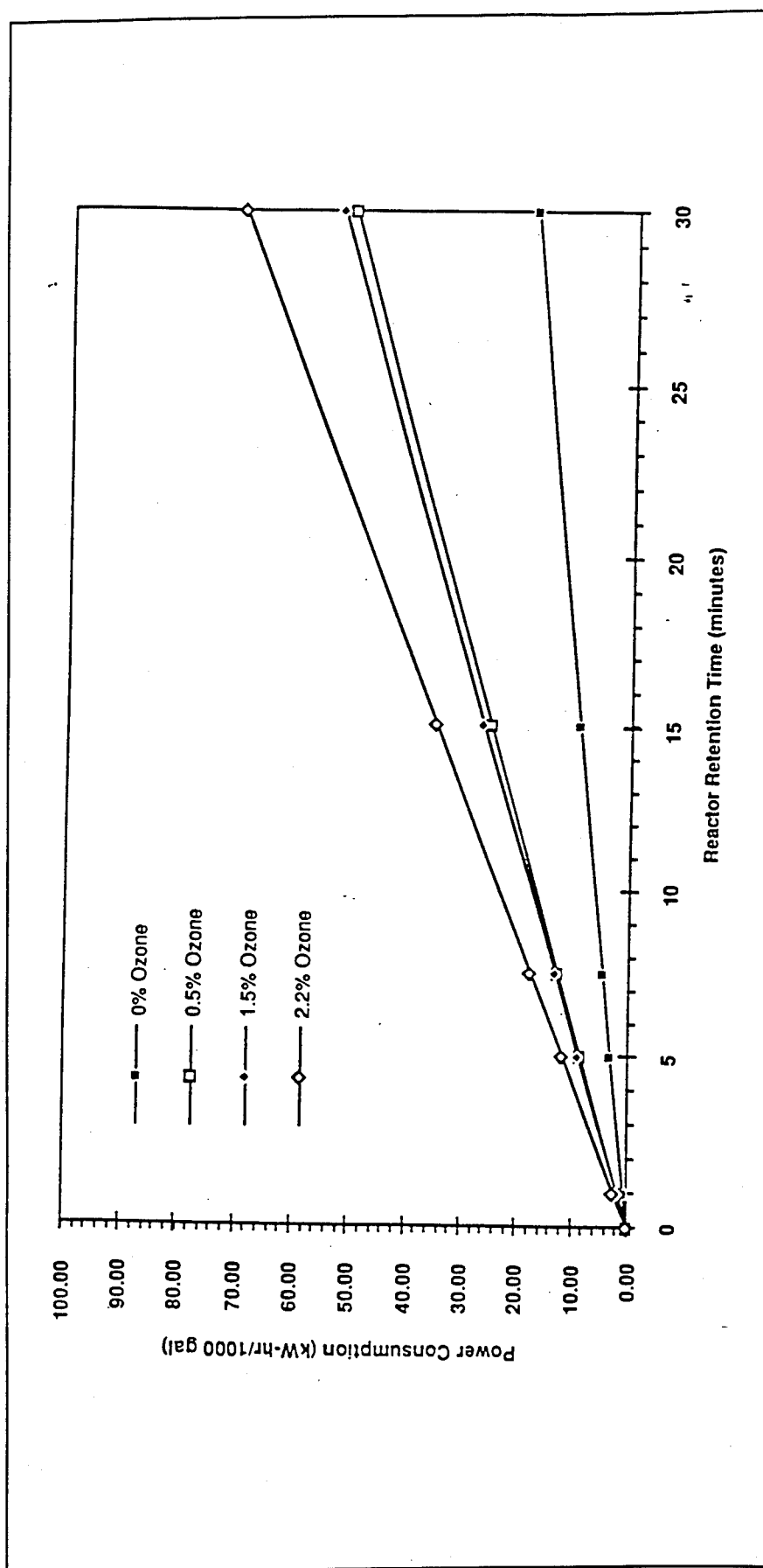
Figure 21. Power consumption versus reactor residence time for four ozone levels

6 Economic Comparison of Carbon Adsorption versus UV/ChO for Treating Picatinny Waters

An economic analysis was performed to determine the most cost-effective method for treating Picatinny waters. A more detailed presentation of the economic analysis for both technologies is presented in Bricka and Fleming (in preparation). Both UV/ChO and carbon adsorption were effective in treating Picatinny waters to the desired levels. The cost analysis included anticipated capital expense and anticipated annual operating expense.

The cost analysis was evaluated for the following conditions:

a. Projected design flow = 1 million gal/day (MGD).

b. Optimum water flowrate from pilot-scale evaluation = 5 gpm.

c. Residence time = 3.75 min.

d. Air flow rate to ozone generator = 190 scfh.

e. Ozone concentration = 0.5 percent.

Ozone Generator Sizing

In the pilot-scale evaluation, optimum conditions of 0.5-percent ozone at a 3.75-min residence time (obtained at 5 gpm) were determined. Using these conditions, the theoretical ozone dosage used in the pilot-scale evaluation was determined and used to size the ozone generator for a 1-MGD treatment facility. The ozone generator required was 300 lb/day.

UV Reactor Sizing

Using a 3.75-min residence time for a 1-MGD plant, the required reactor vessel volume was 2,600 gal.

Capital Costs

The cost for the above-described equipment is approximately $510,000, based upon telephone conversations with Mr. Jack Zeff of Ultrox, Inc. The cost for installation was estimated at approximately 15 percent of the equipment cost. For supervision, inspection, and overhead, the cost is generally estimated to be 6 percent of the equipment cost. For contingency, approximately 10 percent of the equipment cost was estimated. The total capital costs for the system was estimated to be $684,000.

Annual Operating Expense

The anticipated operating expense for the above-described reactor was approximately $0.23/1,000 gal, based upon a telephone conversation with Mr. Jack Zeff of Ultrox, Inc. Typical operating costs run from $0.15 to $0.20 per 1,000 gal (Roy 1990). Operating 24 hr per day equates to $223.00 per day for a 1-MGD facility. This total includes electrical consumption, equipment maintenance, lamp replacement, etc. The total cost per year for the carbon system, including the cost for regeneration and disposal, using regenerated carbon is $52,238/year and for virgin carbon is $86,688/year. A more detailed presentation of the economic analysis is presented in Bricka and Fleming (in preparation).

7 Conclusions Based Upon the Bench- and Pilot-Scale Evaluations

Based upon the bench- and pilot-scale evaluations, the following conclusions have been reached.

General Conclusions

a. RDX cannot be destroyed through chemical oxidizer treatment alone.

b. RDX can be destroyed by UV photolysis alone, by UV photolysis with hydrogen peroxide addition, and by UV photolysis with ozone.

c. The treatment of Picatinny waters does not promote fouling of the quartz tubing sometimes experienced in other UV photolysis evaluations.

d. RDX concentrations can be reduced from approximately 4.5 μg/L to less than 0.617 μg/L, the detection limit for this study.

Bench-Scale Conclusions

a. The destruction of RDX occurred in less than 1 min in the bench-scale evaluations using UV photolysis alone.

b. Bench-scale evaluation results lead to evaluation of UV/ChO on the pilot-scale level.

Pilot-Scale Conclusions

a. All conditions tested in the pilot-scale study reduced RDX concentrations to less than the detection limit of 0.617 µg/L.

b. The destruction of RDX occurred in less than 3.75 min using UV photolysis alone and UV photolysis with 0.5- and 1.5-percent ozone.

c. Pilot-scale tests verified the results obtained in the bench-scale evaluations.

d. Attempts were made to identify the composition of an unknown peak located on the HPLC chromatograms. The composition of the unknown could not be determined by gas chromatography/mass spectrometry, but it was suggested the compound was possibly a highly polar organic.

e. HPLC chromatograms show further destruction of unknown peaks using UV photolysis with ozone than with UV photolysis alone. There is no appreciable increased destruction efficiency by increasing ozone concentration from 0.5 to 1.5 percent. The increased destruction of unknown peaks using concentrations of ozone less than 0.5 percent would require further investigation.

f. There is an approximately 2.5 times increase in power consumption from UV photolysis alone to UV photolysis with 0.5-percent ozone.

g. Economic evaluations indicated that application of carbon adsorption technologies would be the most cost-effective method of treating Picatinny waters. The total cost per year for regenerated carbon is $52,238/year and for virgin carbon is $86,688/year. The cost for the unit is $469,332.70. The total cost per year for UV/ChO is $89,467/year and the cost for the unit is $683,859.

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Appendix A
Results of HPLC Analysis

Table A1
Peak Area of a Large Unknown Peak Measured by HPLC

Oxidizer Conc.	Residence Time, min	Replicate	Peak Area V-min	Average Peak Area V-min
Well 410				
None	0	1	437,776	
		2	392,884	
		3	435,145	421,935
None	3.75	1	285,586	
		2	280,771	
		3	284,116	283,491
None	8.75	1	228,540	
		2	211,973	
		3	208,364	216,292
None	13.75	1	186,151	
		2	182,006	
		3	164,155	177,437
None	27.50	1	136,751	
		2	140,775	
		3	141,271	139,599
None	0	1	310,342	
		2	367,632	
		3	365,275	347,750
0.5% Ozone	3.75	1	29,149	
		2	42,374	
		3	49,266	40,263
0.5% Ozone	8.75	1	32,112	
		2	54,272	
		3	40,097	42,160
0.5% Ozone	13.75	1	28,861	
		2	31,239	
		3	42,212	34,104
0.5% Ozone	27.50	1	28,287	
		2	31,243	
		3	31,746	30,425

(Sheet 1 of 3)

Table A1 (Continued)

Oxidizer Conc.	Residence Time, min	Replicate	Peak Area V-min	Average Peak Area V-min
Well 410 (Continued)				
None	0	1	360,842	
		2	364,155	
		3	362,996	362,664
1.5% Ozone	3.75	1	40,907	
		2	36,250	
		3	47,322	42,493
1.5% Ozone	8.75	1	33,710	
		2	37,746	
		3	46,865	39,440
1.5% Ozone	13.75	1	34,350	
		2	60,329	
		3	45,690	46,789
1.5% Ozone	27.50	1	42,967	
		2	41,785	
		3	44,791	43,180
1383 Water Treatment Facility				
None	0	1	286,053	
		2	269,923	
		3	284,979	280,318
None	3.75	1	176,499	
		2	176,997	
		3	192,707	182,068
None	8.75	1	134,771	
		2	201,745	
		3	119,505	152,007
None	13.75	1	93,148	
		2	98,145	
		3	122,161	104,484
None	27.50	1	79,373	
		2	69,959	
		3	73,307	74,213

(Sheet 2 of 3)

Appendix A Results of HPLC Analysis

Table A1 (Concluded)

Oxidizer Conc.	Residence Time, min	Replicate	Peak Area V-min	Average Peak Area V-min
1383 Water Treatment Facility (Concluded)			
None	0	1	268,456	
		2	291,956	
		3	285,541	281,984
0.5% Ozone	3.75	1	55,731	
		2	41,772	
		3	51,429	49,643
0.5% Ozone	8.75	1	187,676	
		2	32,185	
		3	34,516	
0.5% Ozone	13.75	1	39,157	
		2	39,231	
		3	33,190	37,192
0.5% Ozone	27.50	1	34,560	
		2	39,330	
		3	33,003	35,631
None	0	1	261,805	
		2	282,251	
		3	283,166	275,740
1.5% Ozone	3.75	1	42,358	
		2	51,438	
		3	52,521	48,772
1.5% Ozone	8.75	1	35.617	
		2	44,619	
		3	36,110	38,815
1.5% Ozone	13.75	1	44,273	
		2	36,008	
		3	41,850	40,710
1.5% Ozone	27.50	1	40,630	
		2	60,007	
		3	50,333	50,323

(Sheet 3 of 3)

Table A2
Peak Area of a Large Unknown Peak Measured by HPLC in the Verification Runs

Oxidizer Conc.	Residence Time, min	Peak Area, V-min
None[1]	0	447,501
		442,185
		260,857
Well 410		
0.5% Ozone	3.75	59,258
	6.25	43,579
	8.75	35,800
	11.75	29,003
	13.75	19,171
1383 Water Treatment Facility		
0.5% Ozone	3.75	46,756
	6.25	33,595
	8.75	32,178
	11.25	33,891
	13.75	26,167

[1] Three replicates were conducted.

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13. ABSTRACT (Maximum 200 words)

Due to past operations, soils at some military installations have been contaminated with explosives. Past military operations have included production, testing, and disposal of explosive products. This report presents results of a study conducted at the Picatinny Arsenal, which was established in the 1800's. Production of explosives at the site has ceased, but as a result of the past activities, contaminants are migrating into the groundwater due to contaminant transport from the soils.

Two technologies were evaluated for the treatment of groundwater contaminated with explosives: ultraviolet/chemical oxidation (UV/ChO) and granular activated carbon adsorption. This report presents the results of the UV/ChO study conducted to determine whether low levels of cyclotrimethylene-trinitramine (RDX) and cyclotetramethylene-tetranitramine (MHX) in the drinking water supply at the site could be treated to the required levels. The concentrations of RDX and HMX in the drinking water supply, sampled from well 410 at the site, are approximately 6 and 2 $\mu g/L$, respectively. In the 1980's, RDX and HMX were below health advisory levels. Health advisory levels were lowered in November 1988 by the U.S. Environmental Protection Agency (USEPA) to 2 and 400 $\mu g/L$ for RDX and HMX, respectively. The health advisory standards are expected to be adapted as new drinking water standards. HMX concentrations were approximately 2 $\mu g/L$, well below the health advisory standard of 400 $\mu g/L$. But, RDX concentrations exceeded the proposed standard of 2 $\mu g/L$.

(Continued)

14. SUBJECT TERMS

Catalysts	Ozone	RDX
Hydrogen peroxide	Photolysis	Ultraviolet/chemical oxidation
Oxidizers	Picatinny Arsenal	Ultrox

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Preliminary studies and bench-scale studies were conducted to determine whether UV/ChO should be evaluated on the pilot-scale level. Bench-scale studies included three evaluation scenarios: ozone and hydrogen peroxide as oxidizers, UV photolysis alone (without the use of an oxidizer) using two lamp intensities, and two lamp intensities with ozone and hydrogen peroxide. Based upon the results of the bench-scale evaluation, optimum conditions for treatment evaluations on the pilot-scale level were selected.

For pilot-scale evaluations, ozone and low intensity UV lamps were evaluated. Two locations were selected for the pilot-scale evaluation. Sampling events revealed that well 410 contains the highest concentrations of RDX, ranging from 4.4 to 6.3 μg/L. Water from well 410 is pumped to a drinking water treatment plant used to remove iron, manganese, and trichloroethylene. The full-scale treatment plant may be located at well 410 or at the treatment facility, so treatment evaluations were conducted at both locations. Results of the pilot-scale study indicated destruction of RDX occurred in less than 3.75 min using UV photolysis alone and UV photolysis with 0.5- and 1.5- percent ozone.